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ANALYTICAL ABSTRACTS

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JOURNALS

The following journals and publications were abstracted during 1956.

A.M.A. Archives of Industrial Health.
Acta Chemica Scandinavica.
Acta Chimica Academiae Scientiarum Hungaricae.
Acta Endocrinologia [Copenhagen].
Acta Medica Biologica.
Acta Pharmacologica et Toxicologica [København].
Acta Physiologica Academiae Scientiarum Hungaricae.
Acta Physiologica Scandinavica.
Acta Technica Academiae Scientiarum Hungaricae.
Acta Vitaminologica.
Actas Bioquímicas, Santa Fé.
Afinidad.
Aluminium.
American Dyestuff Reporter.
American Journal of Clinical Pathology.
American Journal of the Medical Sciences.
American Perfumer and Essential Oil Review.
American Society of Brewing Chemists. Proceedings.
Analele Institutului de Cercetări Agronomice al României.
Anales de la Asociación Química Argentina.
Anales de Bromatología.
Anales de Edafología y Fisiología Vegetal [Madrid].
Anales de la Real Sociedad Española de Física y Química, Serie B.
Analyst.
Analytica Chimica Acta.
Analytical Chemistry.
Angewandte Chemie.
Annales des Falsifications et des Fraudes.
Annales Pharmaceutiques Françaises.
Annales Universitatis Mariae Curie-Skłodowska.
Annali di Chimica [Rome].
Annali della Facoltà di Agraria [Università Cattolica del S. Cuore].
Annali della Sperimentazione Agraria [Rome].
Annual Report of the Agricultural and Horticultural Research Station [Long Ashton, Bristol].
Antibiotics and Chemotherapy.
Applied Microbiology.
Applied Spectroscopy.
Aptechnoe Delo.
Archiv für das Eisenhüttenwesen.
Archiv für experimentelle Pathologie und Pharmakologie.
Archiv der Pharmazie.
Archives of Biochemistry and Biophysics.
Archives Internationales de Pharmacodynamie et de Thérapie.
Arhiv za Kemiju.
Arkiv för Kemi.
Arquivos de Bromatologia.
Arzneimittel-Forschung.
Atomics.
Australian Journal of Agricultural Research.
Australian Journal of Applied Science.
Automobile Engineer.

Berichte der deutschen keramischen Gesellschaft.
Biochemical Journal.
Biochemische Zeitschrift.
Biochimica et Biophysica Acta.
Biokhimiya.
Bitumen, Teere, Asphalte, Pech.
Boletín Informativo del Instituto Nacional del Carbon.
Boletín de la Sociedad Chilena de Química.
Boletín de la Sociedad Química del Perú.
Bollettino della Società Italiana di Biologia Sperimentale.
Bollettino Scientifico della Facoltà di Chimica Industriale Bologna.
Brauerei.
Brauwelt, B.
Brauwissenschaft.
Brennstoff-Chemie.
British Medical Journal.

JOURNALS

British Welding Journal.
Bulletin de l'Académie Polonaise des Sciences, Classe Troisième.
Bulletin of the American Society for Testing Materials.
Bulletin of the Chemical Society of Japan.
Bulletin of the Geological Survey of Great Britain.
Bulletin on Narcotics, United Nations, Department of Social Affairs.
Bulletin of the National Hygienic Laboratory, Tokyo.
Bulletin of the Ohio Engineering Experimental Station.
Bulletin der schweizerischen Akademie der medizinischen Wissenschaften.
Bulletin de la Société de Chimie Biologique.
Bulletin des Sociétés Chimiques Belges.
Bulletin de la Société Chimique Belgrade.
Bulletin de la Société Chimique de France.
Bulletin of the United States Bureau of Mines.

Canadian Journal of Biochemistry and Physiology.
Canadian Journal of Chemistry.
Canadian Journal of Medical Technology.
Canadian Journal of Technology.
Canadian Mining and Metallurgical Bulletin.
Canadian Paint and Varnish Magazine.
Cereal Chemistry.
Československá Farmacie.
Chemical Products.
Chemické Listy.
Chemické Zvesti.
Chemikerzeitung.
Chemický Průmysl.
Chemisch Weekblad.
Chemische Berichte.
Chemische Technik [Berlin].
Chemist Analyst.
Chemistry & Industry.
Chimia [Switzerland].
Chimica e l'Industria.
Chimie Analytique.
Chimie et Industrie.
Clinical Chemistry.
Coal Tar [Japan].
Coke and Gas.
Collection of Czechoslovak Chemical Communications.
Comptes Rendus de l'Académie Bulgare des Sciences.
Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences.
Conserva.
Contributions. Boyce Thompson Institute for Plant Research.
Current Science.

Dansk Tidsskrift for Farmaci.
Deutsche Apotheker-Zeitung.
Deutsche Lebensmittel-Rundschau.
Dissertation Abstracts.
Doklady Akademii Nauk SSSR.
Drug Standards.

Endocrinology.
Erdöl und Kohle.
Ernährungsforschung.
Experientia.
Experimental Medicine and Surgery.

Farbe und Lack.
Farmaceutisk Revy.
Farmaco, Scienza e Tecnica [Pavia].
Faserforschung und Textiltechnik.
Fermentatio.
Fette, Seifen, Anstrichmittel.
Food Research.
Food Technology [Champaign].
Fortschritte der chemischen Forschung.
Fuel [London].

JOURNALS

Gesundheits-Ingenieur.
Glas-Email-Keramo-Technik.
Glastechnische Berichte.
Grasas y Aceites.

Helvetica Chimica Acta.
Hilgardia.
Holz als Roh- und Werkstoff.
Hoppe-Seyler's Zeitschrift für physiologische Chemie.
Hutnické Listy.

Indian Journal of Dairy Science.
Indian Journal of Pharmacy.
Industrial Chemist and Chemical Manufacturer.
Industrie de la Parfumerie.
Industries Agricoles et Alimentaires [Paris].
Información de Química Analítica.
Institute of Petroleum Review.
Instituto del Hierro y del Acero.
Instruments and Automation.
International Sugar Journal.

J. "Stefan" Institute Reports [Ljubljana].
Japan Analyst.
Jernkontorets Annaler.
Journal of Agricultural and Food Chemistry.
Journal of the American Ceramic Society.
Journal of the American Chemical Society.
Journal of the American Leather Chemists' Association.
Journal of the American Oil Chemists' Society.
Journal of the American Pharmaceutical Association, Scientific Edition.
Journal of Animal Science.
Journal of Applied Chemistry [London].
Journal of the Association of Official and Agricultural Chemists.
Journal of Biological Chemistry.
Journal of Chemical Education.
Journal of Chemical Physics.
Journal of the Chemical Society [London].
Journal of the Chemical Society of Japan, Industrial Chemistry Section.
Journal of the Chemical Society of Japan, Pure Chemistry Section.
Journal de Chimie Physique.
Journal of Clinical Endocrinology and Metabolism.
Journal of Clinical Pathology.
Journal of Colloid Science.
Journal of Dairy Science.
Journal of Dental Research.
Journal of the Electrochemical Society.
Journal of the Electrochemical Society of Japan.
Journal of Endocrinology.
Journal of Experimental Biology.
Journal of Histochemistry and Cytochemistry.
Journal of the Indian Chemical Society.
Journal of the Indian Chemical Society. Industrial and News Edition.
Journal of the Indian Institute of Science, Section A.
Journal of Inorganic and Nuclear Chemistry.
Journal of the Institute of Brewing.
Journal of the Institute of Petroleum.
Journal of the Iron and Steel Institute.
Journal of Laboratory and Clinical Medicine.
Journal of Nuclear Energy.
Journal of the Oil and Colour Chemists' Association.
Journal of the Optical Society of America.
Journal of the Osaka City Medical Center.
Journal of the Pharmaceutical Society of Japan.
Journal of Pharmacy and Pharmacology.
Journal of Photographic Science.
Journal of Physical Chemistry.
Journal de Physique et le Radium.
Journal of Polymer Science.
Journal für praktische Chemie.
Journal and Proceedings of the Institute of Chemists [India].
Journal of Research and Development. British Cast Iron Research Association.

JOURNALS

Journal of Research. National Bureau of Standards.
 Journal of the Rubber Research Institute of Malaya.
 Journal of the Science of Food and Agriculture.
 Journal of Science of the Hiroshima University, Series A.
 Journal of Scientific and Industrial Research, Section A [India].
 Journal of Scientific and Industrial Research, Section B [India].
 Journal of Scientific and Industrial Research, Section C [India].
 Journal of Scientific Instruments.
 Journal of the Society of Glass Technology.
 Journal of the Society of Leather Trades' Chemists.
 Journal of the Textile Institute, Proceedings and Abstracts.
 Journal of the Textile Institute, Transactions.

Kältetechnik.
 Klinische Wochenschrift.
 Kumamoto Medical Journal.
 Kumamoto Pharmaceutical Bulletin.

Laboratory Practice.
 Lancet.
 Landwirtschaftliche Forschung.

Maataloustieteellinen Aikakauskirja.
 Magyar Kémiai Folyóirat.
 Meddelanden från Finska Kemistsamfundet.
 Meddelelser fra Norsk Farmaceutisk Selskap.
 Melliand Textilberichte.
 Memoria de la XVII Conferencia Anual del Asociación de Técnicos Azucareros de Cuba.
 Metal Industry [London].
 Metallurgia [Manchester].
 Metallurgie.
 Metallurgie und Giessereitechnik.
 Mikrochimica Acta.
 Mitteilungen aus dem Gebiete der Lebensmitteluntersuchung und Hygiene [Bern].
 Mitteilungen der Versuchsstation für das Gärungsgewerbe.
 Monitor de la Farmacia y de la Terapéutica [Madrid].

Nature [London].
 Naturwissenschaften.
 New England Journal of Medicine.
 New Zealand Journal of Science and Technology, B.
 Nippon Kinzoku Gakkai-Shi.
 Nucleonics.

Official Digest of the Federation of Paint and Varnish Clubs.
 Optik.
 Österreichische Chemiker-Zeitung.
 Olii Minerali, Grassi e Saponi, Colori e Vernici.

Paint Manufacture.
 Paint Technology.
 Paintindia.
 Pharmaceutica Acta Helvetiae.
 Pharmaceutical Bulletin [Japan].
 Pharmaceutical Journal.
 Pharmaceutisch Weekblad voor Nederland.
 Pharmazeutische Zentralhalle für Deutschland.
 Phosphorsäure.
 Photoelectric Spectrometry Group Bulletin.
 Pitture e Vernici.
 Plastics Monographs.
 Plating.
 Prace Instytutów Ministerstwa Hutnictwa.
 Proceedings of the American Society of Sugar Beet Technologists.
 Proceedings. Australian Pulp and Paper Industry Technical Association.
 Proceedings of the Indian Academy of Sciences, Section A.
 Proceedings of the Koninklijke Nederlandse Akademie van Wetenschappen.
 Proceedings of the Society for Experimental Biology and Medicine.
 Przegląd Odlewnictwa.
 Przemysł Chemiczny.
 Przemysł Rolny i Spożywczy.
 Pyrethrum Post.

JOURNALS

- Rapport du Commissariat à l'Energie Atomique, Centre d'Etudes Nucléaires de Saclay.
 Recueil des Travaux Chimiques des Pays-Bas.
 Reports of the Atomic Energy Research Establishment [Harwell].
 Reports of the Industrial Research Institute, Asaka Prefecture.
 Reports of the Scientific Research Institute [Japan].
 Research.
 Review of Scientific Instruments.
 Revista de la Asociación Bioquímica Argentina.
 Revista de Ciencia Aplicada.
 Revista Española de Fisiología.
 Revista de la Sociedad Argentina de Biología.
 Revue des Fermentations et des Industries Alimentaires.
 Revue de l'Institut Français du Pétrole et Annales des Combustibles Liquides.
 Revue de Métallurgie.
 Revue Universelle des Mines.
 Reyon, Zellwolle und andere Chemiefasern.
 Ricerca Scientifica.
 Rivista dell' Istituto Sieroterapico Italiano.
 Roczniki Chemii.
 Sakharnaya Promyshlennost.
 Sanitalk.
 Scandinavian Journal of Clinical and Laboratory Investigation.
 Schweizer Archiv für angewandte Wissenschaft und Technik.
 Science [New York].
 Science et Industries Photographiques.
 Sewage and Industrial Wastes.
 Sheet Metal Industries.
 Sheffield University Fuel Society Journal.
 Shikoku Acta Medica.
 Shirley Institute Memoirs.
 Slévárenství.
 Soil Science.
 South African Industrial Chemist.
 Spectrochimica Acta.
 Sperimentale.
 Stärke.
 Suomen Kemistilehti.
 Svensk Kemisk Tidskrift.
 Technische Mitteilungen Krupp.
 Technology Reports of the Tôhoku Imperial University.
 Tin Uses.
 Tonindustrie-Zeitung und keramische Rundschau.
 Transactions of the British Ceramic Society.
 Transactions of the Faraday Society.
 Transactions of the Institution of the Rubber Industry.
 Ukrainskii Khimicheskii Zhurnal.
 Verfkroniek.
 Vestnik Slovenskega Kemijskega Društva.
 Vide.
 Vitamins [Japan].
 Water and Sewage Works.
 Zavodskaya Laboratoriya.
 Zeitschrift für analytische Chemie.
 Zeitschrift für angewandte Physik.
 Zeitschrift für anorganische (und allgemeine) Chemie.
 Zeitschrift für die gesamte innere Medizin und ihre Grenzgebiete.
 Zeitschrift für Erzbau und Metallhüttenwesen.
 Zeitschrift für Lebensmittel-Untersuchung und -Forschung.
 Zeitschrift für Naturforschung.
 Zeitschrift für Vitamin-, Hormon- und Fermentforschung.
 Zhurnal Analiticheskoi Khimii.
 Zhurnal Obshchei Khimii.
 Zhurnal Prikladnoi Khimii.

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 Refera
 Review
 Sugar
 Trans
 Water

JOURNALS

ACKNOWLEDGEMENTS

The organisations publishing the following journals are thanked for allowing reproduction of some abstracts.

British Baking Industries Research Association Abstracts.

British Cotton Industry Research Association. Summary of Current Literature.

Chemical Abstracts.

Fuel Abstracts.

Journal of the Institute of Petroleum.

Journal of the Iron and Steel Institute.

Nutrition Abstracts and Reviews.

Physics Abstracts.

Referativnyi Zhurnal Khimii.

Review of Current Literature relating to the Paint, Colour, Varnish and Allied Industries.

Sugar Industry Abstracts.

Transactions of the British Ceramic Society.

Water Pollution Abstracts.

ERRATA

VOL. 2, 1955.

Abstract No.

Line

- 2631 4 for Palwick read Pawlick.
2770 1 for B. Kawamura read F. Kawamura.
3005 40 for trichloride read chloride.
Index, p. cxii, under **Germanium**, "calorimetric determination" should read "colorimetric determination."
Index, p. c, the entry "**Complexone II**" should read "**Complexone I**."

VOL. 3, 1956.

Abstract No.

Line

- 57 3 for Slévarenstui read Slévarenstvi.
70 14 for Sb'' read Sb'''.
160 3 for Hotoshi read Hitoshi.
177 2 for M. V. Tsao read M. U. Tsao.
224 2 for C. C. Neto read C. Costa Neto.
236 2 for Khainovksy read Khainovsky.
245 23 Delete "more" after "≈."
264 2 for Parish read Parrish.
312 2 for Masabumi read Masafumi.
325 4 for S. Singh read Sarwan Singh.
335 3 for Bouzo read Bouza.
361 2 for Hure read Huré.
426 2 The authors of this paper should be J. Kinnunen and B. Merikanto.
438 2 for J. G. P. Farr read J. P. G. Farr.
470 2 for Yamaji read Yamaguchi.
768 2 for Yuji read Yuzi.
842 3 for 1955 read 1954.
853 2 for Padre read Pádr.
956 17 for W. A. Brooksbank read W. A. Brooksbank, jun.
961 9 for 50 to 55 mm read 50 to 55 cm.
994 2 for d'Amore read D'Amore.
1025 3 for Taichiro read Taitiro.
1058 3 for T. K. H. Otter read I. K. H. Otter.
1082 2 for Yuji read Yuzi.
1083 3 for Yuji read Yuzi.
1130 5 for Šlauf read Šlouf.
1241 2 for M. Whisman read M. L. Whisman.
1257 2 for V. I. Lenskaya read V. N. Lenskaya.
1274 2 for W. N. MacNevin read W. M. MacNevin.
1283 3 for Ginzburg read Ginsburg.
1412 3 for S. H. Götte read H. Götte.
1654 8 for WEFA read WDEA.
1667 2 for R. A. G. de Carvalho read R. A. Guedes de Carvalho.
1697 2 for Kustnetsov read Kuznetsov.
1970 4 for S. Singh read Surgit Singh.
2079 2 for Kawase read Kawane.
2093 2 for Sigeru read Shigeru.
2265 2 for H. J. Goldbach read H.-J. Goldbach.
2514 2 for G. Nitsche read G. Nitschke.
2647 3 for Tashkhodzhaev read Tashkhodzhaev.
2671 3 for Klerstrand read Klevstrand.
2901 2 for I. Otter read I. K. H. Otter.
3114 2 for —, Temme read T. Temme.
3318 4 for Abstr. No. 1932 read Abstr. No. 1132.
3330 8 for $\pm 2 \mu\text{g}$ read $\pm 0.2 \mu\text{g}$.
3383 3 for Vavrejnová read Vavreinová.
3477 2 for A. Červenka read R. Červenka.
3481 3 for N. Hemala read M. Hemala.
3494 2 for Z. Szabó read Z. G. Szabó.
3536 4 for R. Friedel read R. A. Friedel.
3537 5 Insert "[II]" after "Hg."

RR

ANALYTICAL ABSTRACTS

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January, 1956

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ANALYTICAL ABSTRACTS

1.—GENERAL ANALYTICAL CHEMISTRY

1. Analysis for industry. Micro-analytical methods for determining sulphur and the halogens [and other elements]. J. E. Fildes (*Ind. Chem. Mfr.*, 1955, **31** [367], 412-413).—Micro-analytical procedures for determining S, Cl, Br, I, F, As, P, Si, Se and Ti, published since 1950, are reviewed and discussed. (30 references.) S.C.I. ABSTR.

2. Stability of colorimetric reagent for chromium, sym.-diphenylcarbazide, in various solvents. P. F. Urone (Ohio Dept. Health, Columbus, Ohio, U.S.A.) (*Anal. Chem.*, 1955, **27** [8], 1354-1355).—The deterioration and sensitivity of sym.-diphenylcarbazide were studied in a variety of soln. with seven organic solvents. Anhydrous ethyl acetate and acetone soln. were stable for months; ethyl methyl ketone, 2-methoxyethanol and isopropyl alcohol soln. were usable for 1 to 2 weeks, whereas aq. soln. and solvents tending to be basic, such as methanol, ethanol and those containing traces of water and basic impurities, did not make satisfactory stock soln. of the reagent. G. P. Cook

3. Colorimetric determination of pH. G. Monod-Herzen (*Compt. Rend.*, 1955, **240** [22], 2146-2147).—Values of pH between 8.00 and 9.50 are measured, with an accuracy of ± 0.01 and ± 0.04 at the middle and ends of the scale, respectively, by means of a photo-electric cell between which and the source of light is placed a filter that allows only light of wavelength $540 \pm 12.5 \text{ m}\mu$ to pass. The light intensity, measured electrically, is proportional to the pH value of the solution under test, to which a standardised proportion of phenolphthalein is added. S.C.I. ABSTR.

4. Alizarin as alkalinity indicator for Kjeldahl digestions. L. S. Malowan (Univ. Panama, Panama City, Panama) (*Chemist Analyst*, 1955, **44** [3], 75).—Alizarin is pale yellow in conc. H_2SO_4 and intensely blue-violet in solutions of pH > 10 . If about 10 mg of alizarin powder are used in the Kjeldahl-Gunning determination, the colour is stable over the period required for the distillation of NH_3 . Even in the presence of much Fe, e.g., in the determination of N in soil, the colour produced by an excess of alkali is easily visible. Advantages of alizarin over phenolphthalein for this application are indicated. O. M. WHITTON

5. Phenol red-methylene blue mixed indicator. M. R. Verma and V. M. Bhuchar (Nat. Phys. Lab. India, New Delhi, India) (*Chemist Analyst*, 1955, **44** [3], 73).—A mixed indicator—1 drop of 0.1 per cent. phenol red (in 1:1 alcohol) and 2 drops of a 0.02 per cent. aq. soln. of methylene blue for each 100 to 150 ml of solution—gives a very sharp colour transition from green (acid) to violet (alkaline). The intermediate colour, blue, appears at

pH 7.3 and is formed in all transitions from the acid to the basic side and vice versa.

O. M. WHITTON

6. The preparation of carbonate-free alkali-metal, alkaline-earth-metal and tetra-alkylammonium hydroxide solutions. E. Sándi (*Magyar Kém. Foly.*, 1955, **61** [1], 29-30).—These hydroxides, prepared as described, have a Cl^- concn. < 1 per cent. of the OH^- concn.; the CO_3^{2-} content is 1 to 10 per cent. of the Cl^- concn. A 50-ml burette, surmounted by a glass bulb ($\approx 100 \text{ ml}$), is filled with $\approx 50 \text{ ml}$ of Dowex 2. The resin is freed from carbonate by washing with $N \text{ HCl}$ ($\approx 200 \text{ ml}$) at 5 ml per min., from acid with water, and from Cl^- with $N \text{ NaOH}$, followed by a final washing with water to neutrality. Though the column thus prepared is suitable for the prep., from NaCl , of 500 ml of 0.1 $N \text{ NaOH}$, it is better to use a soln. of the alkali-metal, alkaline-earth-metal or tetra-alkylammonium salt (halide) dissolved in 50 to 100 ml of water, sufficient for only 400 ml of 0.1 N soln. The salt soln. is run through the column at 2 ml per min. into a bottle which is kept free of CO_2 . This is followed by sufficient water (at 2 ml per min., increasing to 5 ml per min.) to bring the alkali solution to the required concn. The final soln. is then standardised. The resin can be regenerated with $N \text{ NaOH}$ as described above but, after being washed 4 to 5 times with HCl , can also be used for the removal of CO_3^{2-} . A. G. PETO

7. The influence of organic solvents on adsorption-indicator processes. J. Bognár and S. Sárosi (*Magyar Kém. Foly.*, 1955, **61** [5], 149-154). The effect of organic solvents on adsorption indicators is discussed: the dielectric constant of an organic solvent-water mixture differs from that of water, thus changing the physico-chemical constants connected with adsorption. By using organic solvents of low dielectric constant, the applicability of fluorescein derivatives, e.g., eosin, dibromofluorescein, Rose Bengal, etc., to the argentimetric determination of halogens was greatly extended. Water-dioxan mixtures are particularly suitable; acetone, acetaldehyde and alcohol can also be used. The addition of acetic acid improves the end-point. The error is generally < 0.4 per cent. In acetone-acetic acid ($> 0.2 N$) water, iodide can be determined in the presence of p -dimethylaminobenzylidene-rhodanine, with an accuracy of ± 0.2 per cent. p -Ethoxychrysoidine acts as an acid-base indicator in adsorption processes and thus it is unsatisfactory in a medium of low dielectric constant. A. G. PETO

8. Acidimetry and alkalimetry in non-aqueous media. J. Capilla Rufías and L. Giménez Estellés (*Inf. Quím. Anal.*, 1955, **9** [4], 129-137).—The titration of bases, acids, salts, enols, imides, phenols and alcohols in non-aq. media is reviewed. Some practical applications are tabulated.

L. A. O'NEILL

9. Acidimetric and alkalimetric titrations with dead-stop end-point. G. Mann (Inst. Comm. Qual. Control, Budapest) (*Magyar Kém. Foly.*, 1955, **61** [1], 26-28).—This method is used for acid-alkali titrations in water or an alcohol (methanol, ethanol, *n*-butanol), by adding quinhidrone and measuring the change in the polarising current by means of a galvanometer (range 0 to 8 mV). With a smooth platinum electrode in H_2O , ≈ 0.1 g of quinhidrone per 100 ml is added; neutral salts, colloids, oxidising and reducing agents do not interfere. With an aluminium electrode in H_2O , colloidal and neutral substances do not interfere, but Cl^- , NO_2^- , NO_3^- and other strong oxidising agents do. This method is very accurate for organic acids and bases. The acid and saponification values of vegetable and mineral oils, fats and waxes can be determined accurately, in a benzene-alcohol or benzene-higher polyhydric alcohol soln. A. G. PETO

10. Standardisation of sulphuric acid against sodium carbonate. E. W. Balis, L. B. Bronk, H. A. Liebafsky and H. G. Pfeiffer (G.E.C., Schenectady, N.Y., U.S.A.) (*Anal. Chem.*, 1955, **27** [7], 1173).—Sodium carbonate is a reliable and convenient acidimetric standard; the difference between six commercial samples studied was $< 1:1000$. Normal sulphuric acid is a satisfactory reference standard. A. R. ROGERS

11. Preparation and standardisation of perchloratoceric acid solutions in perchloric acid. G. Frederick Smith (Univ. Illinois, Urbana, Ill., U.S.A.) (*Anal. Chem.*, 1955, **27** [7], 1142-1144).—Perchloratoceric acid in $HClO_4$ is a reagent of very high oxidation potential. As it is stable for only a limited storage time, its preparation in small quantities is desirable. *Procedure*—Dissolve hexanitratammonium cerate (220 g) in H_2O (120 ml) at 60°C. Add 30 per cent. H_2O_2 (25 ml) in small portions, heat to boiling, add conc. HCl (500 ml) in 25-ml portions with intermediate boiling, concentrate to 200 ml, add 70 per cent. $HClO_4$ (240 ml) and boil briskly. Cool, dilute to 500 ml, and electro-oxidise between platinum electrodes at 6 V for 24 hr., with stirring. The final soln. diluted to 600 ml is $\approx 1 F Ce^{IV}$ in 1 F $HClO_4$. Store in an ice-box until ready for dilution with 1 F $HClO_4$ to the desired strength. Standardise against sodium oxalate, with nitroferroin as indicator. A. R. ROGERS

12. Fundamentals of heterometry and their interpretation. M. Bobtelsky (Hebrew Univ., Jerusalem, Israel) (*Anal. Chim. Acta*, 1955, **13** [2], 172-178).—Heterometry is concerned with ptn. reactions and is a process of titration in which the progress of ptn. is plotted as an optical density curve. Such curves often give not only the end-point of the reaction but also an indication of intermediate and subsequent reactions. Heterometry is discussed in relation to turbidimetry, conductimetry, pH and adsorption. W. C. JOHNSON

13. Chronopotentiometric titrations. C. N. Reilley and W. G. Scribner (Univ. N. Carolina, Chapel Hill, N.C., U.S.A.) (*Anal. Chem.*, 1955, **27** [8], 1210-1215).—Chronopotentiometry can be applied to any titration system involving an electro-active constituent. The reactant titrant or product does not need to undergo a reversible electrode reaction, so long as diffusion of the electro-active species is the controlling factor of transition time. The essential apparatus is a convenient source of current, a pH meter and a stop-watch. Chronopotentiograms

obtained with a stationary platinum electrode are more reproducible than polarograms obtained with a rotating electrode, and the method would therefore be useful in the titration of material in low concn. and the analysis of small vol. where reproducible stirring is difficult. Disadvantages are similar to those of amperometric titrations. K. A. PROCTOR

14. Temperature coefficient of the silver electrode potential in solutions initially free from the metal ions. H. Khalifa and I. M. Issa (Fac. Sci., Cairo Univ., Egypt) (*J. Indian Chem. Soc.*, 1955, **32** [6], 383-386).—Potentials set by the silver electrode in universal buffer soln. are less positive by ≈ 0.7 volt than E_0' for the $Ag-Ag_2O$ system. The temp. coeff. measured between 15° and 55° C is high and variable and does not correspond to that of stable systems. E. G. BRICKELL

15. Recent developments in the methods of chromatography and paper electrophoresis. S. Berlingozzi (Univ. Florence, Italy) (*Sperimentale*, 1954, **5** [3-4], 33-52).—A review of paper chromatography and electrophoresis is presented. Chromatography with paper discs, and the application of chromatography to problems of stereochemistry are discussed. The application of unidimensional horizontal chromatography to the photometric determination of amino acids is described in detail, together with some quantitative experiments on the electrophoresis of blood sera. (42 references.) C. A. FINCH

16. Partial acetylation of paper for chromatography. E. M. Buras, jun., and S. R. Hobart (S. Reg. Research Lab., New Orleans, La., U.S.A.) (*Anal. Chem.*, 1955, **27** [9], 1507-1508).—A procedure and apparatus are described for the partial acetylation of paper, in which are used an activation reagent of 5 per cent. acetic anhydride in glacial acetic acid and an acetylation soln. of 4 parts of 22.5 per cent. acetic anhydride in amyl acetate and 0.5 part of 1.8 per cent. $HClO_4$ in glacial acetic acid (by vol.). G. P. COOK

17. Mutual interferences and elimination of calcium interference in flame photometry. J. Spector (Imperial Coll. Trop. Agric., Trinidad, B.W.I.) (*Anal. Chem.*, 1955, **27** [9], 1452-1455).—The well-known mutual cationic interferences of Na, K and Ca in flame photometry, in particular with a Lange flame photometer, are described. A method is given for the elimination of calcium interference by the addition of Al; this addition has little effect on the reading from Na or K, but depresses that of Ca considerably, so making chemical separation unnecessary. K. A. PROCTOR

18. Precision in X-ray emission spectrography. H. A. Liebafsky, H. G. Pfeiffer and P. D. Zemany (Gen. Electr. Co., Schenectady, N.Y., U.S.A.) (*Anal. Chem.*, 1955, **27** [8], 1257-1258).—Under ideal operating conditions, X-ray emission spectrography may be regarded as a random process, and the standard deviation (background assumed negligible) should be equal to the square root of the mean number of counts, as in radioactivity. This has been verified experimentally as well as the fact that, if the actual standard deviation significantly exceeds that predicted, then operating conditions are not ideal. K. A. PROCTOR

19. Effect of cell-circuit resistance in polarography with stationary and dropping electrodes. M. M. Nicholson (Humble Oil and Refining Co.,

Baytown, Texas, U.S.A.) (*Anal. Chem.*, 1955, **27** [9], 1364-1365).—An ohmic drop of several hundredths of a volt, due largely to cell resistance, can change the voltage scanning rate to produce a marked effect on the polarographic current at a stationary electrode. It has been shown by an electromechanical method of instantaneous resistance compensation that this effect accounts for most of the variation in the ratio of max. current to concn. observed in the oxidation of organic sulphides. The compensation system is applicable also to dropping and rotating electrodes. K. A. PROCTOR

20. Improved purification of tetramethylammonium chloride for polarographic studies. P. L. Pickard and W. E. Neptune (Univ. Oklahoma, Norman, Okla., U.S.A.) (*Anal. Chem.*, 1955, **27** [8], 1358).—About 10 g of the technical-grade salt are dissolved in 100 ml of hot 25 per cent. methanol in acetone; the hot soln. is filtered, 100 to 110 ml of acetone are added and the soln. is allowed to cool. The crystalline material is filtered off and dried in a vacuum-desiccator. The yield is 60 to 65 per cent. and is of sufficient purity for use as a supporting electrolyte in aq. or alcoholic media. G. P. COOK

21. Application of radioactivity to chemical analysis. E. Broda and T. Schoenfeld (*Chim. e Ind.*, 1955, **37** [7], 548-559).—A general review of analytical methods based on radiochemistry is presented. These methods include the tracer technique, involving the use of compounds "labelled" with radioactive isotopes, analysis by radioactive reagents, the isotope-dilution method, activation analysis of the sample by irradiation with neutrons, and analysis by neutron absorption. (200 references.) C. A. FINCH

2.—INORGANIC ANALYSIS

22. Some organic reagents in inorganic paper-chromatography. Takio Naito and Niroko Takahashi (*Japan Analyst*, 1954, **3** [2], 125-127).—The use of 1-phenylthiosemicarbazide (I), gallein (II) and thiogallein (III) as detecting agents for inorganic paper-chromatography was studied. When developed with a mixture of acetone and conc. HCl (20:1), or butanol and 5 N HCl (10:5), Cu, Cd, Bi, Ni, Co, Zn, Hg and Fe⁺⁺⁺ can be simultaneously detected with ethanolic soln. of I. The mixture of Sn, As and Sb is developed with the mixed solvent, glacial acetic acid and conc. HCl (9:1) or conc. HNO₃ (4:1), and detected with ethanolic soln. of II or III. K. SAITO

23. Paper-chromatographic study of metal β -diketone chelates. E. W. Berg and J. E. Strasser (Louisiana State Univ., Baton Rouge, La., U.S.A.) (*Anal. Chem.*, 1955, **27** [7], 1131-1134).—Colours and sensitivities are recorded for spot tests of 2-thenoylperfluorobutylmethane (I) and 2-furoylperfluorobutylmethane (II) with common metal ions. Absorption spectra are given for the chelates with Fe^{III}, Cu^{II}, Ni^{II}, Co^{II} and Mn^{II}. These metals may be separated by chromatography of the chelates on Whatman No. 1 paper. With I, the best solvent is light petroleum - methanol (92:8); the R_F values are, respectively, 0.82, 0.77, 0.51, 0.47 and 0.35. With II, sharper zones are obtained with light petroleum - methanol - dioxan (92:7:1); the R_F values are 0.84, 0.77, 0.50, 0.46 and 0.20. The position of the Fe chelate is detected by its yellow

colour; Co, Ni and Cu chelates give yellow, blue and grey - black colours, respectively, with alcoholic dithio-oxamide; the Mn chelate gives a green colour with NaOH and benzidine. A qual. explanation of the observed R_F sequence may be made from solubility and polarisation data. A. R. ROGERS

24. Inorganic salts in non-aqueous solvents. I. Absorption spectra of transition-metal salts in dimethylformamide. R. T. Pflaum and A. I. Popov (State Univ. Iowa, U.S.A.) (*Anal. Chim. Acta*, 1955, **13** [2], 165-171).—Absorption spectra of Cr, Mn, Fe, Co, Ni and Cu salts in dimethylformamide have been determined. The spectra are strongly influenced by the presence of certain anions, the order of decreasing effect being Cl⁻, acetate, NO₃⁻ and ClO₄⁻. The absorption spectrum of CoCl₂ is strongly affected by the addition of water, and the absorption of Cu acetate soln. is markedly decreased. W. C. JOHNSON

25. The determination of small quantities of metal ions using anthranilic acid. F. Holmes and W. R. C. Crimmin (Univ. Coll. N. Wales, Gt. Britain) (*Anal. Chim. Acta*, 1955, **13** [2], 135-141).—When anthranilic acid (0.7 mg) is heated for 1 hr. at 95°C with an excess (25 ml) of 0.01 N perchloratocerate in 2 N HClO₄, 20.9 \pm 0.3 equiv. of cerate are reduced. The excess of cerate is titrated with 0.01 N Na oxalate in 2 N HClO₄, nitroferroin being used as indicator. This method can be used for the indirect determination of Cu and Zn after pptn. of the metals as their anthranilates. It is, however, preferred to redissolve the anthranilates, diazotise the acid in an aliquot and couple with N-1-naphthylethylenediamine. The purple colour that is produced has an absorption max. at 550 m μ . With the Spekker absorptiometer, an Ilford 605 filter and a 1-cm cell, concn. of anthranilic acid in the range 0.64 to 3.84 μ g per ml can be determined. Copper can be separated from Zn⁺⁺ and from other metals normally pptd. by anthranilic acid if the pptn. is carried out in the presence of Na acetate. W. C. JOHNSON

26. The analytical application of -onium compounds. I. Polarographic behaviour of tetramethylammonium iodide towards several metal ions. Mutsuaki Shinagawa and Hiroshi Matsuo (Hiroshima Univ., Japan) (*Japan Analyst*, 1954, **3** [2], 114-120).—Tetramethylammonium iodide (I) was prepared from methyl iodide and aq. NH₃ and its reactions towards a variety of metal ions were tested by means of polarography. Characteristic precipitates are formed between I and Bi, Pb, Sb^{III} and Hg^{II} in dil. HCl (0.1 to 1 N), which appear to contain complex iodo anions (BiI₄⁻, PbI₄⁻, etc.). The mechanism of pptn. and the kinetic current on the polarogram were studied. I can be used as an analytical reagent for Bi, but not for other ions. II. Polarographic behaviour of triphenylselenonium chloride with bismuth. Mutsuaki Shinagawa, Hiroshi Matsuo and Setsuya Isshiki (*Ibid.*, 1954, **3** [3], 199-204).—Triphenylselenonium chloride (II) shows two reduction waves ($E_1 = -0.93$ V and -1.11 V vs. the S.C.E.), the second being dependent on the pH. Reactions between II and various metal ions were tested and it was found that II is specially suitable for the detection and determination of Bi in the presence of I' (limit of detection 0.1 μ g; limit of concn. 1 in 10⁶). The pptn. reaction was studied by means of polarography and amperometric titration. The composition of the ppt. appears to be (C₆H₅)₃SeBiI₄. Bismuth is amperometrically titrated in 0.5 N HCl in the presence of I' with

size and intensity of the spot with standard samples. The lower limit for the estimation is $1 \mu\text{g}$ of Cu^{II} in 0.1 ml of soln. A. G. PERO

39. Iodimetric determination of copper and iron in a mixture. (Application of masking action to volumetric analysis.) Susumu Suzuki and Osamu Aihara (*J. Chem. Soc. Japan, Pure Chem. Sect.*, 1955, **76** [1], 42-44).—Experimental conditions for the simultaneous determination of Fe^{III} , Fe^{II} and Cu with the use of various masking agents were studied. In a mixed soln. with Cu^{II} , Fe^{III} can be quantitatively oxidised by iodine soln. at pH 6 to 7 in the presence of pyrophosphate or tartrate, and its amount determined by titrating the excess of iodine with $\text{Na}_2\text{S}_2\text{O}_3$ soln. In a mixed soln. with Fe^{II} and Fe^{III} , Cu^{II} are determined iodimetrically by masking Fe^{III} with pyrophosphate. The use of NH_4F is also advantageous for the masking of Fe^{III} against reduction by iodide. K. SAITO

40. Thioacetamide in the separation and compleximetric determination of copper and aluminium in alloys. A. M. Amin (Univ. Cairo, Giza, Egypt) (*Chemist Analyst*, 1955, **44** [3], 66-68).—The two procedures given are based on the use of thioacetamide which, under the conditions employed, precipitates Cu completely as its sulphide from a tartrate solution while leaving Al in solution as a tartrate complex. The Cu in the ppt. is determined by titration with EDTA, murexide being used as indicator. The excess of thioacetamide in the filtrate is decomposed with HNO_3 or $\text{K}_2\text{S}_2\text{O}_8$. The Al is then determined volumetrically according to Flaschka by the addition of excess of EDTA and back-titration with either ZnSO_4 soln. (Eriochrome black T as indicator) or with $\text{Th}(\text{NO}_3)_3$ soln. (alizarin S as indicator). O. M. WHITTON

41. The determination of copper in whetlerised carbon following destructive oxidation of carbon employing hot concentrated perchloric acid. G. F. Smith (Univ. Illinois, U.S.A.) (*Anal. Chim. Acta*, 1955, **13** [2], 115-119).—Whetlerised carbon contains 5 to 12 per cent. of copper, which is added to increase its absorptive efficiency, and the following method is used for its analysis. *Procedure*—Reduce a sample to 40 mesh and transfer 1 to 2 g to a 500-ml Vycor conical flask. Add 10 ml of conc. H_2SO_4 , 5 ml of HClO_4 (70 to 72 per cent.), 10 ml of conc. HNO_3 and 25 to 50 mg of $\text{K}_2\text{Cr}_2\text{O}_7$ to serve as a catalyst. Fit a refluxing still-head and fume eradicator and boil the mixture gently until no more brown fumes are evolved. Then raise the temp. until HClO_4 refluxes from not more than three-fourths of the flask-wall height (190° to 200°C) and maintain at this temp. until the carbon is oxidised and the soln. assumes an orange colour through re-oxidation of Cr^{III} to CrO_3 . Boil off the HClO_4 (195° to 200°C) and then add conc. HCl in drops at 5 to 10-sec. intervals until the Cr is volatilised as CrO_2Cl_2 or is reduced to Cr^{III} . Cool, dilute with water, neutralise with aq. NaOH soln. and titrate the Cu^{II} by the standard iodimetric method. The whole procedure occupies 25 to 30 min. W. C. JOHNSON

42. The use of rhodamine B in analytical chemistry. II. The determination of small quantities of gold. B. J. MacNulty and L. D. Woollard (Min. of Supply, Kidbrooke, London) (*Anal. Chim. Acta*, 1955, **13** [2], 154-158).—In the colorimetric determination of Au^{III} with rhodamine B, the concn. of HCl and Cl^- must be closely controlled. *Procedure*

—Add the sample soln., containing $> 30 \mu\text{g}$ of Au^{III} , to a mixture of 2.5 ml of constant-boiling HCl and 5.0 ml of saturated aq. NH_4Cl soln.; then add 5.0 ml of 0.04 per cent. aq. rhodamine B soln. and transfer the mixture to a 75-ml pear-shaped funnel containing 10.0 ml of isopropyl ether. Shake the funnel 100 times, separate the ether layer and measure its absorption with the Spekker absorptiometer and an Ilford 605 filter. Prepare a calibration graph with known quantities of gold. The max. error for $15 \mu\text{g}$ of Au is -10.7 per cent. W. C. JOHNSON

43. Determination of magnesium in alkali products. Photometric method using thiazole yellow. O. A. Kenyon and G. Oplinger (Allied Chem. and Dye Corp., Syracuse, N.Y.) (*Anal. Chem.*, 1955, **27** [7], 1125-1128).—A rapid method for the determination of < 0.1 per cent. of Mg in alkali products is described, based on the production of a lake with Titan yellow in NaCl soln. The concn. of NaCl must be controlled, and Al, Cu, Fe, Mn, Ni and Ca removed. Results are accurate to within 2 to 5 per cent. A. R. ROGERS

44. A new method for nephelometric determinations of small amounts of cadmium with potassium ferrocyanide. A. Petzold and I. Lange (*J. prakt. Chem.*, 1955, **2**, Series IV, [3], 121-126).—A method is described by which small amounts of Cd (0.05 to 0.20 mg) are determined nephelometrically with $\text{K}_4\text{Fe}(\text{CN})_6$. The influence of anions and cations on the formation of turbidity was examined and it has been found that, with the exception of sulphide, cyanide and fluoride, anions have no effect, but the presence of $\approx 1 \text{ mg}$ of Fe^{III} , Mn^{II} , Co^{II} , Ni^{II} , Cu^{II} , Zn^{II} , Al^{III} or Pb^{II} , and $\approx 5 \text{ mg}$ of Ca^{II} or Mg^{II} interferes with the reaction and these metals have to be eliminated. *Procedure*—A neutral solution, containing not more than 0.20 mg of Cd, is treated with 1 ml of 10 per cent. aq. NH_3 and 10 ml of 10 per cent. NH_4Cl diluted to 50 ml and shaken vigorously. After addition of 1 ml of 5 per cent. $\text{K}_4\text{Fe}(\text{CN})_6$ soln., the solution is shaken again and the turbidity formed in 15 to 20 min. is compared with that of standards whose concn. differ by 0.01 mg of Cd. S.C.I. ABSTR.

45. Determination of magnesium in iron. G. Graue, R. Marotz and A. Zöhler (Hüttenwerke Phoenix A.-G., Duisberg-Ruhrort, Ger.) (*Angew. Chem.*, 1955, **67**, 123-126).—The wet determination of < 0.05 per cent. of Mg requires complete separation of heavy metals. This is possible, even without previous ether extraction or electrolysis, by pptn. with $(\text{NH}_4)_2\text{S}$. Traces remaining in soln. are removed by adsorption on $\text{Zr}(\text{OH})_4$. In the filtrate Ca and Mg are pptd. with 8-hydroxyquinoline, the ppt. is redissolved and Mg is determined photometrically with Titan yellow. From 1 to $30 \mu\text{g}$ in 10 ml can be determined within ± 3 per cent. in 8 hr. CHEM. ABSTR.

46. Spectrographic analysis of magnesium in nodular cast iron. A. Rodríguez Pérez and F. Burriel-Martí (*Inst. Hierro Acero.*, 1954, **7**, 345-348).—Working curves for the line pairs Mg 2802.7 - Fe 2813.29 and Mg 2795.54 - Fe 2788.11 were made from chemically prepared standards and applied to the spectrographic analysis of six samples. Comparison with two methods of wet analysis showed that the former pair gave the more consistent results. J. IRON AND STEEL INST. ABSTR.

47. The analysis of metallic nickel. III. Determination of magnesium. Shigeru Yokosuka (Sumitomo Metal Mining Co., Ltd., Japan) (*Japan Analyst*, 1955, 4 [3], 141-144).—The colorimetric determination of a small amount of Mg (> 0.0002 per cent.) in Ni by the use of Titan yellow was suggested for use in factory control. Nickel is removed by electrolysis in H_2SO_4 soln. The influence of common elements, including Cu, Fe, Pb, Zn, Sn and Cd, can be eliminated by adding KCN. The pink colour of Mg in an aqueous soln. of Titan yellow is markedly stabilised by adding starch soln. as protective colloid. *Procedure*—The sample (2 g) is dissolved in HNO_3 (1 + 1, 30 ml), treated with H_2SO_4 (1 + 1, 5 ml) and submitted to electrolysis (4 V, 5 to 6 amp., ≈ 60 min.), a mercury cathode being used. The colourless electrolytic soln. is evaporated to dryness, dissolved in HCl (1 + 1, 3 ml) and water (20 ml), made alkaline with aq. NH_3 soln. (to ppt. Al) and filtered. The filtrate is treated with small amounts of KMnO_4 , MnSO_4 and ethanol at 80°C , and the ppt. of MnO_2 is filtered off. The soln. is again evaporated to dryness and heated at $\approx 500^\circ\text{C}$ for 10 min. to remove ammonium salts. The residue is dissolved in a small amount of HCl, treated with starch soln. (0.2 per cent., 5 ml), hydroxylamine hydrochloride (5 per cent., 1 ml), KCN (1 per cent., 1 ml), Titan yellow (0.15 per cent., 1 ml) and NaOH (1 N, 5 ml), and made up to 50 ml. The extinction is measured at 535 m μ and the content of Mg is calculated. K. SAITO

48. Analytical application of Dutoit's thermovolumetry. I. Analysis of calcium and magnesium in dolomite. K. K. Chatterji (Univ. Coll. of Sci. and Technol., Calcutta, India) (*J. Indian Chem. Soc.*, 1955, 32 [6], 366-370).—A volume correction for temp. change to avoid fictitious breaks in the thermometric curves is given; total temp. change for a const. vol. of the titrant, $(T - T_0) C_v$, being plotted against the vol. of titrant added, whence

$$(T - T_0) C_v = \frac{(T - T_0)(V_0 + \Delta V)}{V_0}$$

Dutoit's method (*J. Chim. Phys.*, 1922, 19, 324) is applicable for Ca and Mg in dolomite. The ore (2.5 to 3 g) is dissolved in conc. HCl, diluted, and ≈ 10 g of NH_4Cl are added. Aqueous NH_3 is then added until Fe, Al and Ti are pptd., when the soln. is filtered, brought to pH 4 with acetic acid and made up to 250 ml. A 50-ml portion of this soln. is titrated thermometrically, first by 0.4859 N ammonium oxalate for Ca and then, after adding 5 ml of conc. aq. NH_3 , with 0.4889 M microcosmic salt for Mg. E. G. BRICKELL

49. Tentative routine method for the determination of lime in magnesite and magnesia refractories. British Ceramic Research Association Chemical Analysis Sub-Committee (*Brit. Ceram. Res. Ass. Spec. Publ.*, 1955, No. 9).—The sample is treated with HCl. The insoluble matter is removed by filtration, evaporated to dryness with HF and H_2SO_4 , fused with Na_2CO_3 , dissolved in HCl and added to the main soln. The Ca is then pptd. as oxalate from a soln. of pH ≈ 6 , a high oxalate concn. being used to minimise co-pptn. of Mg and to prevent pptn. of metals of the ammonia group. The filtered ppt. is redissolved in HCl and the Ca is re-pptd. The ppt. is filtered off and dissolved in H_2SO_4 and the hot soln. is titrated with 0.1 N KMnO_4 . With 3 per cent. of CaO present, the reproducibility is ± 0.1 per cent. of CaO.

BRIT. CERAM. ABSTR.

50. Determination of trace elements in zinc blende. F. Hegemann and H. Kostyra (Techn. Hochschule, Munich, Ger.) (*Metall*, 1954, 8 [19-20], 768-772).—Trace elements in zinc blende are spectrographically determined by the arc (dispersion) method. A mixture of test material and spectral graphite powder, 1:1 by wt., is most suitable for recording the emission spectra generally over the first 40 sec. of the ignition. The reference element is Fe, which is chemically determined in the test samples and, if necessary, is added as Fe_2O_3 in amounts up to 20 per cent. The light intensities are rapidly and visually determined by the standard paper density scale. Elements in amounts of 30 to 0.3 p.p.m. are determined visually to ± 20 to 30 per cent. and photometrically to ± 3 to 12 per cent. A special procedure for determining Tl in amounts > 5 p.p.m. requires buffering with KCl in a wt. ratio of test sample: KCl: graphite of 2:1:1. D. R. GLASSON

51. Compleximetric analysis of zinc-lead ores using thioacetamide and ion-exchange resin. A. M. Amin and M. Y. Farah (Univ. Cairo, Giza, Egypt) (*Chemist Analyst*, 1955, 44 [3], 62-66).—An analytical scheme for complex oxidised zinc-lead ores is presented and details of the procedure are given. After the ore has been dissolved in acid, insoluble lead and calcium sulphates are separated together with silica. The remaining soln., made 2 N in HCl, is passed through Amberlite IRA-400(Cl) resin to remove Zn, which is then eluted with water and 0.025 N HNO_3 , and titrated with EDTA soln. (disodium salt). Iron is separated with cupferron from the acid solution or, alternatively, extracted with ether from a solution 6 N in HCl. Aluminium is separated with aq. NH_3 and NH_4Cl in the usual manner. Manganese and traces of Pb are pptd. as sulphides with thioacetamide, and Ca and Mg are determined by direct titration with EDTA. Results agree well with those of classical methods. O. M. WHITTON

52. New methods for the determination of cadmium. H. Basińska (*Wiadom. Chem.*, 1953, 7 [6], 284; *Referativnyi Zh., Khim.*, 1955, Abstr. No. 5,790).—Volumetric and gravimetric methods for the determination of Cd are based on the interaction of Cd^{++} with $\text{Li}_2\text{Fe}(\text{CN})_6$ to give a ppt. of $\text{Cd}_2\text{Fe}(\text{CN})_6$ (Tananaev and Kozlov, *Brit. Abstr. C*, 1951, 361). The methods are not applicable in the presence of metals that form slightly soluble ppt. with $\text{Fe}(\text{CN})_6^{4-}$; salts of K^+ and NH_4^+ , with which Cd forms complex compounds of variable composition, also interfere. E. HAYES

53. Studies on the chemical analysis of boron. IV. Paper-chromatographic detection of boron in the presence of silver, mercury and lead. Satoru Muto (*J. Chem. Soc. Japan, Pure Chem. Sect.*, 1955, 76 [3], 294-297).—Paper-chromatographic detection of BO_3^{3-} in the presence of Ag, Hg and Pb was studied with 80 per cent. aq. ethanol and solutions of N acids, N bases and M salts as developing agents. The R_f value of BO_3^{3-} is ≈ 0.8 in the presence of Ag and Hg, and ≈ 0.7 in the presence of Pb; the values are almost independent of the developing agent except when this contains NH_3 . The spot of BO_3^{3-} is easily distinguished in the presence of Ag, Hg and Pb, when developed with a mixture of ethanol and water (4:1, by vol.). K. SAITO

54. Determination of traces of boron in silicon, germanium and germanium dioxide. C. L. Luke

(Bell Telephone Labs., Murray Hill, N.J., U.S.A.) (*Anal. Chem.*, 1955, **27** [7], 1150-1153).—A method is described for the determination of 0.1 to 1 p.p.m. of B in Si, Ge or GeO_2 , with an accuracy of ± 10 per cent. The sample is dissolved in aq. NaOH soln., sodium silicate or germanate is removed by pptn. with methanol, and the B is isolated by distillation as methyl borate and determined photometrically with curcumin. With a sample of Si, double pptn. of sodium silicate is necessary, and the B in the two filtrates must be determined separately. With a sample of Ge, 30 per cent. H_2O_2 must be added to the NaOH soln. to effect solution. Special low-boron apparatus and reagents are needed, and a calibration curve must be used to compensate for losses which amount to < 20 per cent. at the distillation stage.

A. R. ROGERS

55. Determination of the solubility product of metal hydroxide precipitates. I. Reaction of aluminium ions with the hydroxyl ion. Z. G. Szabó, L. J. Csányi and M. Kávai (Univ. Szeged, Hungary) (*Z. anal. Chem.*, 1955, **146** [6], 401-414).—The solubility product of metal hydroxides is calculated from results of potentiometric titrations of the salt solutions with alkali hydroxides using an antimony electrode, the initial pptn. being nephelometrically controlled. The earlier graphical extrapolation method is not quite accurate for evaluating the results; determination of the limiting value of the first differential quotient curve is preferred. The values of the solubility products thus obtained for $[\text{Al}^{+++}][\text{OH}]^3$ are 1.25×10^{-33} at 20°C and 1.92×10^{-32} at 30°C , and for $[\text{H}^+][\text{AlO}_2^-]$ are 1.80×10^{-13} at 20°C and 1.34×10^{-13} at 30°C .

D. R. GLASSON

56. EDTA determination of aluminium, lead and zinc in bronze and brass. J. Kinnunen and B. Merikanto (Outokumpu Oy, Metalworks, Pori, Finland) (*Chemist Analyst*, 1955, **44** [3], 75-77).—Procedures are described for commercial or control analyses of Al, Pb and Zn in brass and bronze. Of these, the following is applicable only when very small amounts of Fe are present. **Copper**—To a soln. of 0.25 g of the sample in 10 ml of HNO_3 (1 + 1) is added ≈ 0.05 g of sulphamic acid. After being boiled until brown gases are no longer evolved, the soln. is cooled and titrated with ≈ 0.08 N $\text{Na}_2\text{S}_2\text{O}_8$ after adding KI and starch. **Aluminium, manganese and lead**—To the soln. remaining after the titration for Cu are added an excess (≈ 0.5 ml) of $\text{Na}_2\text{S}_2\text{O}_8$ soln., a measured excess of 0.04 M EDTA soln. and 0.1 g of ascorbic acid. The soln. is boiled, then 25 ml of 20 per cent. KCN soln. are added, to prevent interference from Cu, Ni, Co and Zn, followed by 10 ml of conc. aq. NH_3 . The excess of EDTA in the cooled soln. is titrated with 0.05 M MnSO_4 (Eriochrome black T as indicator) to give the sum of Al, Mn and Pb. These metals can be determined individually in this titrated soln. **Aluminium**—Triethanolamine (20 ml) is added to the soln., which is then boiled, and the liberated EDTA is titrated with 0.04 M MnSO_4 (Eriochrome black T as indicator). **Lead**—Sodium diethyldithiocarbamate soln. (5 per cent.) (5 ml) is added to the titrated soln., and the liberated EDTA is titrated with 0.005 M MnSO_4 (Eriochrome black T). **Zinc**—To the cooled soln. from the titration for Al is added 4 per cent. formalin and titration with 0.04 M EDTA (with Eriochrome black T as indicator) is carried out to a blue end-point. Further formalin is added and, if the indicator becomes red, further EDTA is added. These additions are

repeated until a permanent blue end-point is obtained. Any Cd in the sample is titrated with the Zn. In a second procedure described, elements that interfere with the determination of Al are removed with a mercury cathode; the method given above for Al can then be used. O. M. WHITTON

57. Determination of high aluminium contents in cast iron without the use of the mercury cathode. B. Bieber and Z. Večeřa (*Stěvdrenstůl*, 1954, **2** [7], 206-210).—Aluminium contents of 1 to 25 per cent. are determined by first removing silica and graphite from a solution of the sample in sulphuric acid and pptg. part of the Fe with NaHCO_3 in the presence of hydrazine sulphate, and the remaining Fe with 1-nitroso-2-naphthol. Aluminium is determined as Al_2O_3 pptd. from the filtrate with aq. NH_3 soln. The method is modified in the presence of Cr, but can be used if the molar Cr:Al ratio is ≥ 1 . J. IRON AND STEEL INST. ABSTR.

58. Photometric determination of gallium with rhodamine B. H. Onishi and E. B. Sandell (Univ. Minnesota, U.S.A.) (*Anal. Chim. Acta*, 1955, **13** [2], 159-164).—Gallium is separated from most other metals, and from all those that yield a colour reaction with rhodamine B, by extracting it with isopropyl ether from 7 M HCl containing TiCl_3 . Subsequently the rhodamine-B compound of Ga is extracted from 6 M HCl with benzene, and since the extraction coefficient under the conditions of the method is only 0.57, accurate vol. measurement is essential. **Procedure**—The sample soln. (5 to 10 ml) must contain 0.5 to 10 μg of Ga and must be 7 M with respect to HCl. Add 2 ml of 20 per cent. TiCl_3 soln. previously extracted with isopropyl ether; if more than 100 mg of Fe^{III} are present more than 2 ml of TiCl_3 are necessary. After 5 min. extract with 8 to 10 ml of peroxide-free isopropyl ether, repeat the extraction with 5 ml of isopropyl ether and rinse the funnel with a further 1 ml. Shake the combined extracts with a mixture of 1 ml of 7 M HCl and 0.5 ml of TiCl_3 soln. for 10 sec., separate, repeat this extraction and then extract with 1 ml of 7 M HCl. Filter the ethereal soln., if necessary, through glass wool, add 0.3 ml of aq. NaCl soln. (1 + 10) and evaporate the ether. Dissolve the residue in 5-0 ml of 6 M HCl and transfer to a dry funnel. Add 0.40 ml of a 0.50 per cent. soln. of rhodamine-B hydrochloride in dil. HCl (1 + 1) and 0.1 ml of aq. hydroxylamine hydrochloride (1 + 10). Add 10.0 ml of benzene, shake for 1 min., and separate. Filter the benzene layer through glass wool and measure its transmittancy at 565 $\text{m}\mu$. Prepare a blank by the same procedure and prepare a calibration curve with known quantities of Ga.

W. C. JOHNSON

59. Coulometric titration of thallous ion with electrogenerated ferricyanide ion. A. M. Hartley and J. J. Lingane (Harvard Univ., Mass., U.S.A.) (*Anal. Chim. Acta*, 1955, **13** [2], 183-188).—Thallous ions are titrated coulometrically with ferricyanide, which is generated by the electrolytic oxidation of ferrocyanide at constant current. Consideration of the redox potentials of the two systems involved shows that the titration is feasible only in alkaline soln. The optimum concn. of NaOH is 2 M and, for the particular apparatus used (cf. *Anal. Abstr.*, 1955, **2**, 300), the optimum concn. of $\text{K}_3\text{Fe}(\text{CN})_6$ is 0.05 M. The reagent blank is reduced to a small constant value by excluding light and de-aerating the soln. before titration. For 4 to 40 mg of Tl in 125 ml of soln. the titration times vary from 123 to

615 sec., currents of 16 to 22 mA being used. The end-point is determined potentiometrically with the use of a platinum indicator-electrode and an S.C.E. The accuracy and precision are 0.2 per cent. An amperometric method for end-point detection is also described.

W. C. JOHNSON

60. The determination of small amounts of thallium in lead. Extraction of thallium (III) chloride with isopropyl ether. K. Lounamaa (Bolidens Gruvaktiebolag, Skelleftehamn, Sweden) (*Z. anal. Chem.*, 1955, **147** [3], 196-198).—Thallium (0.05 to 1 per cent.) in lead may be determined with an accuracy of ± 2 per cent. by oxidation to Tl^{III} , extraction with isopropyl ether and iodimetric titration. Procedure—Dissolve the sample (containing 0.5 to 2 mg of Tl) by warming it with HBr. Dilute with HCl (1:1) to 100 ml, filter off and wash the ppt. with HCl (1:1). Extract the filtrate and washings with isopropyl ether (3 \times 20 ml). Evaporate the extract to dryness, and heat to fuming with H_2SO_4 (1 ml) and $HClO_4$ (2 ml). Cool, and add H_2O (25 ml) and bromine water (25 ml). Remove the excess of Br with 0.1 ml of 25 per cent. phenol in acetic acid, add 1 per cent. KI soln. (3 ml) and 2 per cent. starch soln. (1 ml) and titrate with 0.001 N $Na_2S_2O_3$ from a micro-burette.

A. R. ROGERS

61. Spectrophotometric determination of cerium after oxidation to quadrivalent cerium with lead dioxide. L. Gordon and A. M. Feibush (Univ. Chem. Dept., Syracuse, N.Y.) (*Anal. Chem.*, 1955, **27** [7], 1050-1051).—A rapid and accurate method is described for the determination of Ce, based on the oxidation to Ce^{IV} in H_2SO_4 soln. with PbO_2 , treatment with excess of Fe^{II} , and estimation of the unchanged Fe^{II} by the colour with *o*-phenanthroline. Interference is caused by Cl^- , Mn and V, but not by Th or the rare earths. Procedure—To the sample (containing 20 to 1000 μg of Ce^{III}) add conc. H_2SO_4 (2 to 4 ml), dilute to 10 to 25 ml and add PbO_2 (0.3 g). After 5 min., filter through sintered glass into a soln. of $Fe(NH_4)_2(SO_4)_2$ in 0.5 N H_2SO_4 (10 ml of a known concn. in the range 0.001 to 0.01 N). Add 0.1 per cent. *o*-phenanthroline soln. (10 ml) and enough aq. NH_3 to turn the soln. red. Cool, adjust the pH to between 2.5 and 2.8, and dilute to 100 ml. Compare the extinction at 505 $m\mu$ in a 1-cm cell with that of a Ce-free blank similarly treated, and calculate from a calibration curve.

A. R. ROGERS

62. [Chromatographic] separation of rare-earth elements. M. Lederer (Institut du Radium, Paris, France) (*Nature*, 1955, **176**, 462-463).—Separations of rare earths as free ions can be successfully made by descending paper-chromatography, with a mixture (9 + 1, by vol.) of ethanol and 2 N HCl as solvent. The chromatogram is run for 3 to 5 days. The spots are revealed by spraying with hydroxyquinoline and viewing the fluorescence under u.v. light. Complete separations (into distinct spots) of mixtures of La - Y, La - Dy, La - Yb and La - Eu - Y are reported. Migration of the free ions is not proportional to the ionic radii, but is a max. near Dy - Y. The procedure will separate Ce, Pm and Eu from fission products.

W. J. BAKER

63. Quantitative spectrographic analysis of other rare-earth elements in lanthanum oxide. Ryohei Ishida (*J. Chem. Soc. Japan, Pure Chem. Sect.*, 1955, **78** [2], 171-173).—The sample of La_2O_3 , obtained by the ignition of the pptd. oxalate, is mixed with three times its weight of carbon powder and pressed

into a briquette. A spark is struck between the briquette and a carbon electrode (9000 V, 0.0033 μF , 0.8 mH) and the spectrum is recorded on a photographic plate (exposure 5 min.) by means of a Littrow-type spectrograph. The lines of Ce (4012.4 Å), Pr (3908.0, 3908.4), Nd (4247.37) and Sm (3609.5) are compared with those of La. No significant interference results from the band spectra of CN and C. This method appears to be suitable for the determination of impurities within the range 0.3 to 3 per cent.

K. SAITO

64. High-frequency combustion - volumetric determination of carbon in metals. E. L. Simons, J. E. Fagel, jun., E. W. Balis and L. P. Pepkowitz (G.E.C., Schenectady, N.Y.) (*Anal. Chem.*, 1955, **27** [7], 1119-1122).—An examination has been made of the variables present in the method in which the Lindberg high-frequency combustion furnace and volumetric carbon determinator is used for the determination of C in metals (*Brit. Abstr. C*, 1952, 375). By correcting for variations in gas temp. and barometric pressure during a run, maintaining internal pressure equilibrium, and keeping the burette walls scrupulously clean, the coefficient of variation for a single 1-g sample is reduced to 0.005 per cent. of C. When analysing samples containing < 1 per cent. of C, the weight should be made up to 1 g with a low-carbon steel of known carbon content.

A. R. ROGERS

65. Use of capillary trap in micro-determination of carbon. B. D. Holt (Argonne Nat. Lab., Lemont, Ill., U.S.A.) (*Anal. Chem.*, 1955, **27** [9], 1500-1501).—A rapid and precise manometric method for the measurement of CO_2 produced by combustion in the micro-determination of C is described. The unit described is an adaptation of Smiley's capillary trap (*Anal. Chem.*, in the press) to the standard combustion procedure. At the very low level, 1 μg of C corresponds to a manometer reading of 4 mm, and with sacrifice of precision the measuring unit may be revised to accommodate micro and macro amounts of C. Analysis of steel and ferrosilicon gave results within ± 0.0004 per cent. at the ≈ 0.02 per cent. level.

G. P. COOK

66. Direct titration of carbon dioxide. L. Blom and L. Edelhäusen (Centraal Lab., Staatsmijnen in Limburg, Netherlands) (*Anal. Chim. Acta*, 1955, **13** [2], 120-128).—Methods and applications of CO_2 determination are briefly reviewed. For the determination of CO_2 in air and in combustion products the CO_2 is first absorbed in acetone or pyridine; it is then titrated with a standard soln. of Na methoxide in methanol, thymol blue being used as indicator. In the micro-determination of C in organic compounds the error is generally < 0.7 per cent. of the amount of C present.

W. C. JOHNSON

67. The chemical analysis of calcium cyanamide. I. A modification of the silver picrate method for the determination of dicyandiamide. Hideya Inaba (*Japan Analyst*, 1954, **3** [2], 107-111).—Harger's silver picrate method for the determination of dicyandiamide in Ca cyanamide has been re-examined and a modification is suggested. Melamine and guanidine are also pptd. as picrates, resulting in values too high for the content of dicyandiamide. To avoid this defect, Ag picrate monocyanoguanidine is pptd. with a known excess of $AgNO_3$ soln. (5 per cent.) (> 10 ml for 0.15 g of the sample), which is back-titrated in the supernatant liquid with KSCN soln. II, III. A rapid determination of dicyandiamide and urea by decomposition with

nitric acid. Hideya Inaba (*Ibid.*, 1954, 3 [2], 111-114; [3], 195-196).—Dicyandiamide reacts quant. with dil. HNO_3 in a sealed vessel to give amidinourrea nitrate at 100°C (15 min.). Urea (normally present in calcium cyanamide) is also capable of reacting with dil. HNO_3 in a sealed vessel to give NH_4NO_3 and CO_2 ; this reaction proceeds quant. at 120°C within 3 hr. Calcium cyanamide (4 g) is extracted with acetone (250 ml) and two 50-ml portions of the extract are treated with 0.25 N HNO_3 (15 ml) in a sealed vessel, one at $100^\circ \pm 3^\circ\text{C}$ for 15 min. and the other at 120°C for 3 hr. The excess of HNO_3 is titrated with 0.25 N NaOH to methyl red. The amounts of both components are calculated from the following empirical formulae: N, as urea (per cent.) = $0.499 \times (B-A)$; N, as dicyandiamide = $1.75A - 0.131(B-A)$, where A and B are the volumes (in ml) of 0.25 N HNO_3 consumed by the reactions at 100°C and 120°C , respectively. **IV. A rapid determination of cyanamide nitrogen.** Hideya Inaba and Daiji Yanagisawa (*Ibid.*, 1954, 3 [3], 196-199).—To avoid the interference of melamine in the determination of cyanamide nitrogen, the following modification is suggested. The sample (0.2 g) is treated with NH_4NO_3 (1.0 g), water (100 to 150 ml) and 0.1 N ammoniacal AgNO_3 soln. (40.0 ml) (in the presence of melamine add 10 ml of aq. NH_3 soln., sp. gr. 0.9) for 5 min., with vigorous shaking. The ppt. is filtered off, washed with water and then dissolved in 0.1 N HNO_3 , for titration with 0.1 N KSCN. The time for one estimation is < 20 min. K. SAITO

68. Estimation of silicon in the presence of fluorine. Application to phosphate rock and wet-process phosphoric acid. S. Harel, E. R. Herman and A. Talmi (Fertilizers and Chemicals Ltd., Haifa, Israel) (*Anal. Chem.*, 1955, 27 [7], 1144-1147).—For the estimation of Si in the presence of F, steam-distil from a soln. in HClO_4 to which has been added a known wt. of SiO_2 (as sodium silicate soln.); determine the Si in the distillate (which is free from interfering elements) volumetrically, and the SiO_2 remaining in the flask (free from F) gravimetrically before and after ignition with HF. The Si in the distillate is determined as follows. To a 200-ml aliquot of the steam-distillate add 0.5 per cent. phenolphthalein soln. (3 drops), 0.2 N HCl (20 ml), KCl (10 g) and 6 per cent. KF soln. (10 ml), cool to 0°C , neutralise rapidly with 0.2 N NaOH, heat to 80°C and titrate with 0.2 N NaOH. For accurate work on phosphate rock, an intermediate alkaline fusion and second distillation are necessary. An alternative procedure is based on the pptn. of Si as K_2SiF_6 , followed by titration with NaOH at 80°C ; Al and Fe^{III} interfere. A. R. ROGERS

69. Determination of germanium in low concentrations. M. Senegačnik, L. Kosta and F. Krašovec (*Vestnik Slovensk. Kemijsk. Društ.*, 1955, 2 [1], 9-16).—Some recent methods for the separation and determination of Ge have been investigated. With oxidised haematoxylin the results are influenced by the NH_4Cl formed by the neutralisation of acid in the final solution. More accurate and reproducible results are obtained with phenylfluorone (I). An absorption curve for the Ge - I complex is obtained by subtracting that for I alone from that for the Ge - I complex + excess of I. An extraction procedure based on the solubility of GeCl_4 in CCl_4 is found to be reliable and is applied to zinc concentrates. In the concn. range 0.01 to 0.001 per cent., Ge can be determined with an average deviation of results of < 5 per cent. from the mean. A. B. DENSHAM

70. The detection of a micro amount of germanium by means of an anion-exchange resin saturated with haematoxylin. Hidetake Kakihana, Yoshihiro Mori and Kazuo Yamasaki (*J. Chem. Soc. Japan, Pure Chem. Sect.*, 1955, 76 [2], 215-217).—Amberlite IRA-411(Cl) (≈ 30 mesh) is digested in an acidic soln. of haematoxylin (20 mg in 20 ml of 0.05 N HCl containing 2 ml of ethanol). The yellow resin is put into a drop (0.06 ml) of the sample soln. on a spot plate, and in the presence of Ge (in 0.1 to 3 N HCl) a violet to black coloration appears on the surface of the resin. The limit of detection is $0.003\text{ }\mu\text{g}$ and the limit of concn. is $0.05\text{ }\mu\text{g}$ per ml. Interference results from Fe^{III} , Sb^{III} , Cu^{II} and Sn^{II} , but can be eliminated (except that from Sn) by passing the sample soln. through a column of a cation-exchange resin before the test. K. SAITO

71. Oxidations with alkaline permanganate using formic acid for back-titration. III. Determination of lead and thallium. I. M. Issa and R. M. Issa (Cairo Univ.) (*Anal. Chim. Acta*, 1955, 13 [2], 108-114).—Ions of Pb^{II} (< 0.6 mg) and Tl^{I} (< 0.9 mg) are determined by mixing soln. containing them with an excess of KMnO_4 in the presence of N NaOH and Ba^{II} and titrating potentiometrically the excess of KMnO_4 with standard formic acid (*cf. Anal. Abstr.*, 1954, 1, 1807; 1955, 2, 885). In mixtures of Pb^{II} and Tl^{I} , quantities of Tl^{I} < 30 mg can be titrated directly with standard KMnO_4 in the presence of 0.1 N NaOH if the Pb is first pptd. as PbSO_4 in the presence of telluric acid, or the Pb is pptd. twice as PbSO_4 and the Tl^{I} are titrated in the combined filtrates. W. C. JOHNSON

72. Determination of titanium in titanium metal. R. A. Papucci (F. C. Broeman and Co., Cincinnati, Ohio, U.S.A.) (*Anal. Chem.*, 1955, 27 [7], 1175-1176).—A rapid (80 min.) and accurate method is described for the direct determination of Ti in high-purity Ti and Ti alloys. The Eberbach "Dynacath" high-speed magnetic mercury cathode is used to eliminate the interfering metals Cr, Mo, Fe, Sn, Co, Ni, Cu and Mn. *Procedure*.—Dissolve the sample (0.2 g) by heating with dil. H_2SO_4 (100 ml), cool, filter, add 3 per cent. H_2O_2 (50 ml), evaporate to fuming, cool, boil for 5 min. with H_2O (75 ml), cool, electrolyse for 15 min. at 10 to 15 amp. and dilute to 200 ml. To a 2-ml aliquot add dil. H_2SO_4 (70 ml) and 3 per cent. H_2O_2 (5 ml); dilute to 100 ml and compare the yellow colour ($425\text{ m}\mu$) with that of a standard soln. A. R. ROGERS

73. Weighing quadrivalent titanium chloride for quantitative chemical analysis. I. J. Dzikowski and R. G. Novak (Crane Co., Chicago, Ill., U.S.A.) (*Anal. Chem.*, 1955, 27 [7], 1194).—Accurate sampling of TiCl_4 for quant. analysis is difficult because it is easily hydrolysed. A procedure in which 60-ml serum bottles and hypodermic syringes are used is described, which facilitates syringe and weighing of samples and enables solution of the samples in acid solvent to be carried out in a controlled manner. A. R. ROGERS

74. Rapid titrimetric determination of thorium with fluoride using SPADNS [2(p-sulphophenylazo)-1:8-dihydroxynaphthalene-3:6-disulphonic acid]. G. Banerjee (Darjeeling Gov. Coll., India) (*Z. anal. Chem.*, 1955, 146 [6], 417-422).—A rapid titrimetric determination of Th, in amounts of 5 to 88 mg, has been developed. The test solution is buffered with Na acetate - HCl to pH 3.0, before adding 2 ml of

0.02 per cent. SPADNS indicator, diluting to 50 ml and finally titrating with standard NaF solution until the colour matches a blank containing the buffered indicator solution; the colour change is from blue - violet to scarlet red. A calibration curve relating the titre of the fluoride solution (0.1385 M) to known thorium contents is prepared. Interferences of various cations and anions have been studied, and the quantitative nature of the zirconium interference is confirmed. D. R. GLASSON

75. Direct compleximetric titration of zirconium with Versene using SPADNS [2(p-sulphophenylazo)-1:8-dihydroxynaphthalene-3:6-disulphonic acid]. G. Banerjee (Darjeeling Gov. Coll., India) (*Z. anal. Chem.*, 1955, **147** [2], 105-111).—Zirconium is determined by titration with disodium EDTA (I) in the presence of Na p-sulphophenylazochromotropic acid (II); a 1:1 zirconium (I):I complex is formed and the reaction is stoichiometric. *Procedure*—To a soln. containing 9 to 36 mg of Zr, 2 drops of a 0.4 per cent. soln. of II are added and the volume is made up to 50 ml with 0.01 M HCl soln.; the pH should be within the range 2 to 2.2. The soln. is titrated against a 0.05 M soln. of I until the colour changes from crimson - pink to orange - red. The method can be used in the presence of Ce, La and U, and interference due to Fe^{II} and Fe^{III} can be eliminated by adding ascorbic acid before titration. Ions of Ag, Cu^{II}, Sn^{II}, Ni^{II}, Mo^{III}, Sb^{III}, Bi^{III}, Ce^{IV}, Sn^{IV} and Ti^{IV}, and F⁻, MoO₄²⁻, SO₄²⁻, WO₄²⁻, citrate, oxalate, tartrate and alginate interfere. E. HAYES

76. The chemistry of thorium. Spectrophotometric determination of thorium as the naphthazarin complex. T. Moeller and M. Tecotzky (Illinois Univ., Urbana, Ill., U.S.A.) (*Anal. Chem.*, 1955, **27** [7], 1056-1058).—Naphthazarin (5:8-dihydroxy-1:4-naphthoquinone) (I) gives a purple complex with Th⁴⁺ in ethanol. The complex is a stable cation, in which the ratio of I:Th is 2:1. It absorbs strongly at 570 and 618.5 mμ. The colour is detectable at concn. of Th as low as 1 p.p.m. Beer's law is obeyed at 620 mμ in the concentration range 10⁻⁶ to 10⁻⁸ M, and the formation of the complex is the basis of a spectrophotometric determination of Th⁴⁺ in the absence of uranyl, zirconyl, titanyl and rare-earth-metal ions. A. R. ROGERS

77. Determination of thorium and of rare-earth elements in cerium earth minerals and ores. M. K. Carron, D. L. Skinner and R. E. Stevens (U.S. Geol. Survey, Washington, D.C.) (*Anal. Chem.*, 1955, **27** [7], 1058-1061).—A procedure is described for the quant. pptn. of the oxalates of Th and the rare-earth elements from samples in which the cerium-group elements predominate. The pptn. is carried out from homogeneous soln. at pH 2 by the addition of a soln. of anhyd. oxalic acid in methanol in the presence of Ca²⁺ as carrier. The Ca is removed by pptg. Th and rare-earth elements as hydroxides with aq. NH₃ at pH > 10. The Th is then separated by pptn. of the sebacate at pH 5, and the rare-earth elements in the filtrate may be pptd. with aq. NH₃ at pH 9. The method requires 0.5 to 2 g. of sample; the max. error for the combined thorium and rare-earth oxides is ± 0.6 mg, and for the separated thorium is ± 0.5 mg. A. R. ROGERS

78. High-frequency titrations involving chelation with ethylenediaminetetra-acetic acid. IV. Complexation of thorium nitrate. R. Hara and P. W.

West (Louisiana State Univ., U.S.A.) (*Anal. Chim. Acta*, 1955, **13** [2], 189-194).—When a soln. of Th(NO₃)₄ is added to a soln. of EDTA a complex is formed in the ratio Th:EDTA = 1:1 and the Th(NO₃)₄ added can be determined by a high-frequency titration of the H⁺ liberated. It is preferred, however, to conduct a high-frequency titration of Th(NO₃)₄ with a standard soln. of the disodium salt of EDTA. A sharp break in the titration curve appears when no further liberation of H⁺ occurs. The optimum concn. range of Th(NO₃)₄ is 0.0002 to 0.001 M, and 0.003 to 0.04 M disodium salt of EDTA is used as titrant. In a vol. of 100 ml, 7.7 to 9.2 mg of Th⁴⁺ are titrated with an error of 0.5 per cent. The presence of Ba²⁺, Sr²⁺, Ag⁺, Tl⁺ and the alkali metals, and electrolytes in general, reduces the sensitivity of the method. Acetate, oxalate, fluoride and most heavy metals interfere seriously. W. C. JOHNSON

79. Conductimetric method for rapid chemical analysis of the nitric acid - nitrogen dioxide - water system. D. M. Mason, L. L. Taylor and S. P. Vango (Calif. Inst. Techn., Pasadena, Calif., U.S.A.) (*Anal. Chem.*, 1955, **27** [7], 1135-1142).—For the rapid determination of concn. of NO₂ and H₂O in fuming nitric acid, measurements of specific conductance are made at 0°C for the sample alone and for a duplicate sample saturated with anhyd. KNO₃. Data are presented in graphical and tabular form for calculating composition in the ranges 0 to 12 per cent. w/w of NO₂, 0 to 10 per cent. w/w of H₂O, and 12 to 20 per cent. w/w of NO₂, 0 to 6 per cent. w/w of H₂O. Both NO₂ and H₂O can be determined on an absolute basis to ± 0.3 per cent. w/w in the composition range studied. Impurities cause less error in the determination of H₂O than occurs by conventional chemical analysis. A. R. ROGERS

80. Volumetric determination of hydrazine hydrate. J. Brandštetr (Vojenska Tech. Akad., Brno, Czech.) (*Chem. Zvesti*, 1954, **8**, 261-266).—Alkalimetric titration of hydrazine hydrate (I) results in values too high because NH₃ forms in the decomposition of I. It is recommended that NH₃ be determined from the difference of alkalimetric and oximetric titrations. These results agree with determinations of NH₃ in I by distillation. For alkalimetric titration HCl (0.5 N) is best; for oximetric titration 0.1 N KMnO₄ in dil. H₂SO₄ with KBr is preferable after completing the alkalimetric determination. CHEM. ABSTR.

81. The spectrophotometric determination of phosphorus with amidol. F. Capitan Garcia and F. Martinez Alvarez (Inst. Edafol. y Fisiol. Vegetal, Granada, Spain.) (*An. Edafol. Fisiol. Veg.*, 1954, **13** 767-790).—Amidol (diaminophenol hydrochloride) (I) when used alone to reduce molybdophosphoric acid to molybdenum blue produces a max. absorption at 700 mμ. Beer's law is applicable up to 5.4 p.p.m. of P₂O₅. Use of I alone without heat is not recommended; on heating to 60°C the reaction is speeded up but the sensitivity is decreased. Addition of Na₂SO₃ (10 per cent. in 0.5 N H₂SO₄) to I produces max. absorption at 820 to 830 mμ and Beer's law holds up to 22 p.p.m. An excess of I has no influence on the results. *Procedure*—To the test soln. in a 100-ml flask add 10 ml of molybdate soln. and 10 ml of I soln. Shake vigorously. Dilute to 100 ml with H₂O. Set aside for 1 hr. and measure the absorption at 820 to 830 mμ in a spectrophotometer or use a red filter with a photometer. Calculate p.p.m. of P₂O₅ from

a standard curve. The molybdate soln. is prepared by dissolving 50 g of $(\text{NH}_4)_2\text{MoO}_4$ in 300 ml of H_2O , adding 500 ml of 10 N H_2SO_4 and diluting to 1 litre. To prepare the I soln., dissolve 100 g of Na_2SO_3 in 700 ml of H_2O , add 2 to 5 ml of this soln. to another 100 ml of H_2O and dissolve in it 3 g of I. Mix the two soln. The soln. of I is stable for at least 20 days.

CHEM. ABSTR.

82. Effect of temperature on photometric determination of phosphorus in steel. H. C. Baghurst and V. J. Norman (S. Austral. Defence Stand. Labs., Melbourne) (*Anal. Chem.*, 1955, **27** [7], 1070-1073).—The effect of temp. on the molybdate-vanadate method for the photometric determination of P in steel has been examined. Of the methods of oxidation published (*viz.* perchloric acid, brominated HCl, permanganate, persulphate), only the last gives results independent of temp.; this is attributed to the fortuitous formation of SO_4^{2-} during the reaction. Addition of SO_4^{2-} will stabilise the more convenient permanganate method to the effect of temp., and an accurate procedure has been developed which is applicable to a wide range of alloy and plain carbon steels. *Procedure*—Boil the sample (1 g) with a 4 per cent. soln. of $(\text{NH}_4)_2\text{SO}_4$ in HNO_3 (d 1.160) until nitrous fumes are removed, add 2 per cent. KMnO_4 (5 ml) and boil for 2 min. Add enough solid NaNO_2 (≈ 80 mg) to clear the soln., boil to expel nitrous fumes, cool and dilute to 100 ml. To 50 ml add the colour reagent (30 mg of sodium vanadate and 1 g of sodium molybdate in 10 ml of H_2O), mix and allow to stand for 10 min. Dilute this soln., and the blank (the other 50 ml), to 100 ml, and compare the colours in a Spekker absorptiometer at the same temp., with 4-cm cells and Kodak 543 filters (430 m μ). Calculate the percentage of P from a calibration curve.

A. R. ROGERS

83. Determination of phosphorus in pig and cast iron by the routine nitromolybdate method. W. E. Clarke (*J. Res. Brit. Cast Iron Ass.*, 1955, **5** [12], 630-642).—Methods for dissolving samples more quickly, including addition of NaF, optimum pptg. conditions for molybdophosphate, the time of standing needed to complete pptn., the end-point, and the effects of interfering elements, were investigated by the B.C.I.R.A. Methods of Analysis Sub-Committee, and a standard procedure is recommended. Samples (0.5 to 2 g, according to phosphorus content) are dissolved in HNO_3 and water (40:60). Solution may be expedited by adding a few drops of HF or a little NaF. The resulting solution is filtered through pulp and the filtrate is oxidised with KMnO_4 , boiled to expel SO_3 , and ammonium nitromolybdate reagent (freshly filtered) is added. The ppt. is dissolved in a measured excess of standard NaOH solution and the excess of alkali is back-titrated with standard HNO_3 solution to phenolphthalein.

S.C.I. ABSTR.

84. Colorimetric determination of small quantities of phosphoric acid with vanadate-molybdate. B. Kurnies (*Phosphorsäure*, 1955, **15**, 64-72).—Small quantities of H_3PO_4 (5 to 100 μg in 25 ml) are determined with good results by the vanadate-molybdate method. The plant substance is ashed, 2 ml of 5 N H_2SO_4 are added and heated on a water bath for 30 min. The solution is transferred to a 50-ml flask, 5 ml of NaF soln. (20 mg of F) are added and the mixture is clarified by centrifuging. From the resulting soln. and from a blank prepared similarly 25 ml of each are mixed with 10 ml of a

mixture (1:1:1) of HNO_3 , ammonium vanadate soln. (0.1 per cent.) and ammonium molybdate soln. (2.5 per cent.) and shaken. After half an hour the extinction of the coloured soln. is measured and compared with standard curves.

CHEM. ABSTR.

85. Iron as a disturbing factor in the determination of phosphate by the molybdenum blue method. A. Kaila (Univ. Helsinki) (*Maatalous. Aikakausk.*, 1954, **26**, 159-168).—The interference of Fe^{+++} and Fe^{++} in the determination of phosphate by the Truog and Meyer modification of the molybdenum blue method was studied. In the presence of Fe^{+++} the colour intensity was dependent on the concn. of acid, SnCl_2 and molybdate. Increasing concn. of SnCl_2 prevented the fading at concn. of P < 0.25 p.p.m. Fairly good results were obtained when molybdate (mg per ml) in the soln. was five times as high as the acidity (expressed as normality). With lower molybdate concn. the presence of Fe^{+++} caused an increase in colour intensity, while in higher concn. the fading effect was marked. The same procedures failed to prevent the fading effects of Fe^{++} . This was accomplished by the substitution of HCl for H_2SO_4 .

CHEM. ABSTR.

86. Analytical chemistry of phosphates. II. Influence of temperature and ageing time on the volumetric estimation of pyrophosphate. New volumetric determination of pyrophosphate in presence of ortho- and meta-phosphates. T. Kato, Z. Hagiwara and R. Shinozawa (*Technol. Rep. Tôhoku Univ.*, 1955, **19** [2], 157-166).—The determination of pyrophosphate by pptg. $\text{Zn}_3\text{P}_2\text{O}_7$ from a buffered solution, pH 3.8 to 3.9, dissolving the ppt. in dil. aq. NH_3 and titrating with EDTA was reported previously (*Anal. Abstr.*, 1955, **2**, 3025). It has now been found that, as the temp. rises, the pyrophosphate ppt. slowly dissolves, giving low results, *e.g.*, at $39^\circ \pm 1^\circ \text{C}$ only 98.13 per cent. of the total amount is found. Precipitation is, however, complete at room temp. On standing at $18^\circ \pm 1^\circ \text{C}$ the ppt. gradually becomes colloidal. Provided the standing time is > 4.5 hr. the results are quant., but a standing time of 10 to 30 min. is recommended when making the analysis. This method for the determination of pyrophosphate gives satisfactory results in the presence of ortho- and trimeta-phosphates.

J. M. JACOBS

87. Quantitative infra-red analysis of condensed phosphates. D. E. C. Corbridge and E. J. Lowe (Albright and Wilson Ltd., Birmingham, England) (*Anal. Chem.*, 1955, **27** [9], 1383-1387).—The use of the potassium bromide pressed-disc technique is described for the quant. analysis of condensed phosphates in the form of dry powders. In a four-component mixture, three components could be determined with an accuracy within ± 0.5 per cent. over the range of concn. occurring in commercial material. The method compared favourably in speed and accuracy with X-ray and chemical methods and should be applicable to any phosphate mixtures in which the individual components give reasonably strong, non-overlapping absorption maxima.

K. A. PROCTOR

88. Separation of phosphoric acid and arsenic acid from cations by means of a cation-exchange resin. Yukichi Yoshino (*Japan Analyst*, 1954, **3** [2], 121-125).—Phosphoric acid is separated from most common metal ions (except Fe^{+++} and Al^{+++}) by passing a weakly acidic soln. (≈ 0.1 N HCl) through a column of Amberlite IR-112; the eluate

is titrated with standard NaOH soln. Adsorption of Cr^{+++} on the resin is effected from only a freshly prepared soln. Attempts made to separate PO_4^{+++} from Fe^{+++} and Al^{+++} were not successful. Arsenate can be similarly separated from most metal ions except Fe^{+++} , and titrated iodimetrically in an acidic soln. K. SAITO

89. **The determination of quivalent antimony after reduction by iodine and red phosphorus.** E. A. Johnson and E. J. Newman (Hopkin and Williams Ltd., Chadwell Heath, Essex, England) (*Analyst*, 1955, **80**, 631-632).—The method described is based on that of Fitzgibbon (*Brit. Chem. Abstr. A*, 1933, 921) for the determination of arsenates. The antimonate (0.4 g) is dissolved in 30 ml of dil. HCl (1 + 1) and the hot soln. is treated with 2 ml of 0.1 N I and 0.2 g of red P. The liquid is heated until the supernatant layer is colourless, then filtered while hot through asbestos in a Gooch crucible, and washed with water. The filtrate is treated with 4 g of Na K tartrate and adjusted to only slight acidity with 5 N NaOH. When the filtrate is cold, NaHCO_3 is added and the liquid is titrated with 0.1 N I, starch being used as indicator. A. O. JONES

90. **Iodimetric determination of antimony, arsenic, iron and tin in a mixture. (Application of masking action to volumetric analysis.)** Susumu Suzuki, Kenichi Harimaya and Mamoru Ueno (*J. Chem. Soc. Japan, Pure Chem. Sect.*, 1955, **76** [1], 45-48).—Any binary or tertiary mixture of Sb, As, Fe and Sn can be analysed iodimetrically by changing the pH value at which the soln. is titrated, with or without the aid of masking agents. In an acidic soln. only Sn^{++} are quant. oxidised with iodine soln., As^{+++} are iodimetrically titrated in a weakly acidic or neutral soln. (pH > 4.2), whilst Fe^{+++} and Sb^{+++} are titrated in an alkaline soln. in the presence of fluoride. Citric acid can mask Fe^{+++} but not Sb^{+++} against oxidation with iodine. These masking actions are not affected by the presence of Sn^{++} and As^{+++} . K. SAITO

91. **Analysis by internal electrolysis. Determination of antimony, lead and tin in a type-metal alloy.** P. Ippoliti and E. Scarano (*Ann. Chim., Roma*, 1955, **45** [6-7-8], 492-501).—A complete analysis of a type-metal alloy containing Sb, Sn and Pb is obtained rapidly and accurately (± 0.5 per cent.), with a 20 to 50-mg specimen, by employing internal electrolysis with a variety of electrolytes. A special apparatus (*cf.* Giordani *et al.*, *Ric. Sci.*, 1954, **11**, 2316) with plate anodes of Sn or Pb, or a cylindrical anode of Al, and with an anode-compartment electrolyte of M NaCl and 0.15 M HCl, and a cylindrical cathode of Pt is used. The alloy specimen is treated with conc. HCl (20 ml), which attacks Sn and Pb over several hr.; Sb is dissolved by the addition of KClO_3 . The resulting solution is diluted with water, then treated with hydroxylamine hydrochloride and shaken until no more Cl is liberated, when gelatin (30 mg) is added with boiling water to make up to a vol. of 80 to 100 ml. From this solution Sn is deposited with a tin anode by passing a current for 15 min. at room temp., then for 1 hr. at 60° to 70° C. The resulting solution is made alkaline with NaOH to methyl red, then acetic acid is added to re-acidify. A solution containing Cd^{++} (15 mg) is added, to give a vol. of 150 to 180 ml, and electrolysis is performed with an aluminium anode, for 75 min., from 50° C to the b.p., for the determination of Pb and Cd. Further electrolyses

are carried out similarly, with an anode of Pb and an HCl electrolyte, to determine Sb, and with an anode of Al and acetic acid electrolyte to eliminate residual Pb. Finally the same anode is used with HCl electrolyte to determine Sn. Full practical details are supplied for all these electrolyses.

C. A. FINCH

92. **Rapid electro-analytical separation of bismuth from other metals in sulphuric acid solutions. I. Determination of bismuth.** M. S. Jovanović and S. Dj. Janković (*Bull. Soc. Chim., Belgrade*, 1955, **20** [2], 119-123).—Amounts of 0.05 to 1.0 g of metallic Bi are dissolved, with heating, in 10 ml of conc. H_2SO_4 and diluted to ≈ 150 ml with H_2O . Solutions containing > 0.5 g of Bi remain clear, but at higher concn. a ppt. is formed. Electrolysis is carried out at 70° C, after addition of 5 ml of ethanol to the solution. The p.d. remains constant at 2.0 V (0.6 to 1.6 amp.) until the current strength sinks to 0.1 amp. A further 15-min. electrolysis completes the quant. pptn. of Bi on the cathode. Results show good agreement with theoretical values. II. **Separation of bismuth from tin.** M. S. Jovanović and S. Dj. Janković (*Ibid.*, 1955, **20** [2], 125-131).—Both metals are dissolved in 10 ml of conc. H_2SO_4 and the solution is kept boiling until most of the pptd. sulphur is removed. After cooling, addition of a further 20 ml of H_2SO_4 , H_2O to ≈ 100 ml and 5 ml of ethanol, the Bi is pptd. electrolytically on the copper-plated cathode at 70° C and p.d. 2.0 V, until the current strength sinks to 0.1 amp. A further 15-min. electrolysis completes the quant. pptn. of Bi. The average value for Bi, found by this method, was 99.84 per cent., compared with 99.72 per cent. by volumetric and 99.91 per cent. by gravimetric analysis. Tin is determined subsequently in the same solution, either electrolytically by Sand's method, or with 0.1 N KBrO_3 after reduction with Ni. S.C.I. ABSTR.

93. **Determination of oxygen in metals without high vacuum by capillary-trap method.** W. G. Smiley (California Univ., Los Alamos, New Mexico, U.S.A.) (*Anal. Chem.*, 1955, **27** [7], 1098-1102).—A simple and rapid (12 min.) method which does not require high vacuum is described for the determination of O in metals. The sample (1 to 300 mg) is dropped into molten Pt in a graphite crucible. Any O in the sample reacts to form CO, which is swept out by a stream of argon (100 ml per min.) at atmospheric pressure, oxidised by I_2O_5 , condensed (as CO_2) in a capillary trap and measured with a capillary manometer. Recovery experiments with Cu_2O gave 99 per cent. recovery. The method, which is sensitive to 0.3 μg of O, has been applied to samples of Fe, steel, Al and Th, but was unsuccessful with Ti. A. R. ROGERS

94. **Determination of oxygen in titanium and titanium alloys.** M. Codell and G. Norwitz (Pitman-Dunn Labs., Frankford Arsenal, Philadelphia, U.S.A.) (*Anal. Chem.*, 1955, **27** [7], 1083-1090).—A new method is proposed for the determination of 0.05 to 0.5 per cent. of O in Ti and Ti alloys, based on the reaction $\text{TiO}_2 + 2\text{C} + 2\text{Br}_2 = \text{TiBr}_4 + 2\text{CO}$. The sample (2 g) is mixed with graphite (1.5 g) and treated with bromine at 825° C in a 96 per cent. silica tube, using He as carrier gas (110 ml per min.). The CO produced is oxidised to CO_2 by CuO at 500° C, and the CO_2 is absorbed in Ascarite and weighed. The Br and TiBr_4 are removed by freezing, and the last traces by passing through granular Zn at 350° C. Precautions recommended include drying the Br with conc. H_2SO_4 ; purifying the He

by passing through Cu and CuO at 500° C and then through Ascarite and anhydrous; removal of impurities at the CO stage with Ascarite; removal of H₂O at the CO₂ stage with anhydrous; determination of a blank. The results agree well with those by the vacuum-fusion method for one sample of Ti and three representative alloys. None of the elements commonly found in commercial titanium metal and alloys interferes.

A. R. ROGERS

95. Composition of the barium sulphate precipitate obtained in the presence of excess of ferric chloride. O. P. Sýzganova (*Tr. Kazansk. Khim.-Tekhnol. In-Ta*, 1952, [17], 139-150; *Referativnyi Zh., Khim.*, 1955, Abstr. No. 7,585).—The effect of a 500-M excess of ferric chloride on the pptn. of BaSO₄ in the determination of S in alloys is studied. The best results are obtained by pptn. at 80° C from a soln. containing 1.2×10^{-2} M HCl. Ferric and chloride ions are adsorbed on and occluded in the BaSO₄, and a preliminary separation of Fe is recommended.

E. HAYES

96. Gravimetric determination of small amounts of tellurium in sulphur. A. Aaremae and G. O. Assarsson (Geol. Survey of Sweden, Stockholm) (*Anal. Chem.*, 1955, 27 [7], 1155-1156).—Small amounts of Te in soln. may be determined gravimetrically as the metal by reduction with hydrazine and SO₂ in the presence of HCl. Quant. pptn. is difficult if the concn. of Te is < 0.5 mg per 100 ml; in this case, the Te should be enriched by coprecipitation as tellurous acid with Al(OH)₃. A special glass apparatus is described for the determination of Te in sulphur.

A. R. ROGERS

97. Analysis of complex chromium ions by electrophoresis. I. Qualitative analysis (1). Akira Kawamura, Hiroshi Okamura and Naonori Kaneko (Tokyo Univ. Agric. Tech.) (*Japan Analyst*, 1955, 4 [3], 158-163).—The electrophoretic distribution of the following complex oxalato-chromium ions of various charges was studied (300 to 500 V, 1 hr.): [Cr(H₂O)₄]³⁺, [Cr(H₂O)₄X]²⁺, [Cr(H₂O)₃.X.CH₃CO₂]⁺, [Cr(H₂O)(X)₂]⁺ and [Cr(X)₃]⁰, where X is -OOC-COO-. When developed with N/30 HClO₄, the spots of these complex ions are revealed separately in the above sequence from the cathode to the anode. No significant decomposition of the complex ions takes place during development. The ageing of the complex salt [Cr(H₂O)₄][Cr(X)₃] was studied by this method and it was found that [Cr(H₂O)₄X][Cr(H₂O)₂(X)₂] (a co-ordination isomer) is gradually formed.

II. Qualitative analysis (2). Akira Kawamura and Hiroshi Okamura (*Ibid.*, 1955, 4 [3], 163-166).—The results obtained in Part I (see above) were applied to various complex compounds of Cr which have ligands other than oxalate. The mobilities of chromium complexes that contain NH₃, SCN, SO₄ or OH groups in the ligand are practically identical with those of the oxalate complexes having the same charge. This relationship holds for complexes treated with alkali or by heat, as long as the charge of the complex ion remains unchanged. When a chrome tanning liquor, obtained by the reduction of dichromate with various reducing agents, including glucose, methanol, glycerol, ethanediol and Na₂S₂O₃, is examined by this method, several spots are observed corresponding to differently charged chromium complexes. The charges are dependent not only on the reducing agent but also on the concn. of neutral salts contained in the dichromate soln.

III. Quantitative analysis. Akira Kawamura and

Hiroshi Okamura (*Ibid.*, 1955, 4 [3], 166-171).—The electrophoretic spots of positively charged, uncharged and negatively charged chromium complexes are so clearly separated (500 V, 1 hr.) that Cr can be determined from the spots. The paper is cut and Cr is extracted with water from the areas to be colorimetrically examined. This method can be applied to the analysis of chrome tanning liquors to investigate chromium complexes contained in them.

K. SAITO

98. Determination of chromate ion by the use of an ion-exchange resin and ethylenediaminetetraacetic acid. Kiyoharu Isagai and Nakako Tateshita (Saga Univ., Japan) (*Japan Analyst*, 1955, 4 [4], 222-223).—Chromate ions are pptd. with a known amount of Ba²⁺ in acetic acid soln. and the excess of Ba²⁺ is titrated in an ammoniacal soln. with standard EDTA soln., Eriochrome black T being used as indicator. Since CrO₄²⁻ are not adsorbed on a cation-exchange resin, cations, e.g., of Fe and Cu, are removed by passing the soln. through a column of Amberlite IR-120(H) before the pptn. of BaCrO₄. This method can be applied to the analysis of chromium steel, but is not much better than the conventional method.

K. SAITO

99. Spectrophotometric determination of chromium in copper alloys with diphenylcarbazide. Hiroshi Kitagawa and Yoshito Aimoto (Hitachi Central Research Lab., Japan) (*Japan Analyst*, 1955, 4 [3], 144-148).—The colour extinction of Cr diphenylcarbazide (up to 0.1 mg of Cr per 100 ml of 0.2 N H₂SO₄) at 545 mμ is not affected by the presence of a large amount of Cu (< 0.5 g). Iron (< 0.5 per cent.) is masked by the addition of H₃PO₄; Pb, Sn and As are co-precipitated with MnO₂ produced by the oxidation of Cr with KMnO₄. The time taken for an estimation is < 20 min. The deviation of the result is ± 0.001 per cent. for 0.005 to 0.1 per cent. of Cr. *Procedure*—The sample (0.4 g) is dissolved in HNO₃ (1 + 1, 10 ml) and heated with H₂SO₄ (1 + 1, 2 ml) until white fumes are evolved. The product is diluted to 50 ml and treated with a few drops of KMnO₄ (3 per cent.). The excess of KMnO₄ is decomposed with MnSO₄ (10 per cent., 3 ml) and the ppt. is filtered off. The filtrate is cooled to below 20° C, treated with H₃PO₄ (1 + 1, 1 ml) and a methanolic soln. of diphenylcarbazide (1 per cent., 1 ml), and made up to 100 ml. The extinction is measured within 10 min. at 545 mμ.

K. SAITO

100. Separation of chromium, manganese, iron and nickel by ion-exchange chromatography. D. I. Ryabchikov and V. F. Osipova (*Dokl. Akad. Nauk, SSSR*, 1954, 96, 761-763).—Quantitative separation of Fe-Mn, Cr-Fe, Mn-Cr, Ni-Cr and Fe-Mn-Cr soln. was effected by selective adsorption on ion-exchange resins. Resin KU-2 (Russian made) was the best of five resins tested. Good results were obtained with synthetic mixtures of metals and with industrial samples. Sodium pyrophosphate was added to Mn and Fe^{III} soln. of pH 3 to 4 to form stable [Fe₂(P₂O₇)₃]⁴⁻ which was not adsorbed by the H form of the resin as was Mn. After adsorption the resin was washed with H₂O, and Mn was eluted with 10 per cent. H₂SO₄; this regenerated the resin. To a Cr-Fe soln., KSCN soln. was added and the mixture was heated to form stable [Cr(SCN)₆]³⁻ which, unlike Fe, was not adsorbed by the Na form of the resin. After filtration Fe was eluted with 4 N HCl. Sodium pyrophosphate soln. was added to Cr-Mn soln. of

pH > 7 to form stable $[\text{Cr}_2(\text{P}_2\text{O}_7)_3]^{6-}$ which, unlike Mn, was not adsorbed. After filtration Mn was eluted with 10 per cent. H_2SO_4 . A soln. of chlorides of Fe, Mn and Cr at pH 4 was treated with 10 per cent. $\text{Na}_2\text{P}_2\text{O}_7$ soln. By filtration Cr and Mn were adsorbed and Fe was in the filtrate; Cr and Mn were eluted with 4 N HCl, the washings were evaporated to dryness and 5 per cent. NH_4SCN soln. was added. By filtration through the Na form of the resin only Mn was adsorbed. Separation of Ni-Cr was effected by heating with SCN^- and filtering through the Na form of the resin; Ni was adsorbed and eluted with 4 N HCl. CHEM. ABSTR.

101. Determination of molybdenum and vanadium by the use of a cation-exchange resin. Tsutomu Matsuo and Akio Iwase (Yamagata Univ., Japan) (*Japan Analyst*, 1955, 4 [3], 148-152).—The adsorption and the differential elution of Mo and V were studied with the cation-exchange resins Diaion K and Amberlite IR-120. Both Mo and V exchange well with a cation-exchange resin in an acidic soln. of pH 2. Molybdenum is eluted free from Fe and V with 5 per cent. $\text{NaNH}_2\text{HPO}_4$ soln. (pH 9); V is then eluted with dil. HCl (3 to 4 N) as V^{IV} from a column of Diaion K, but as V^{V} from other resins. Experimental conditions, including the temp., the concn. of reagents and the rate of flow, were studied, as well as the influence of other ions. Tungsten in the form of tungstate is not adsorbed on the resin under the given conditions, and interferes with the adsorption of V; this effect can be masked by the addition of H_3PO_4 (< 2 M). These methods, followed by titration with KMnO_4 , can be applied to the determination of Mo in ferromolybdenum and of V in Cr-W-V steel and in ferrovanadium.

K. SAITO

102. Formation and reduction of molybdophosphoric acid and molybdo-arsenic acid. M. Jean (*Compt. Rend.*, 1955, 240 [23], 2237).—Ions of Bi, Ti and Zr act as catalysts and enable the reduction of molybdo-phosphoric and -arsenic acids to be completed at room temp. It has therefore been found possible to determine P and As at ordinary temp. Optimum conditions are, for the determination of P: acidity of 1.2 N H_2SO_4 , 15 mg of $\text{Bi}_2(\text{SO}_4)_3$ + 0.2 g of Na_2MoO_4 in 50 ml; for As: acidity of 0.4 N H_2SO_4 , 20 mg of $\text{Bi}_2(\text{SO}_4)_3$ + 0.1 g of Na_2MoO_4 in 100 ml. S.C.I. ABSTR.

103. Combustion of tungsten carbide by high-frequency-induced radiant heating. E. L. Simons, J. E. Fagel, jun., and E. W. Balis (G.E.C., Schenectady, N.Y.) (*Anal. Chem.*, 1955, 27 [7], 1123-1125).—Tungsten carbide can be burned rapidly and completely at $\approx 1400^\circ\text{C}$ in a stream of O without the use of a flux by subjecting the sample (200 mg) in a porcelain crucible to the radiation from a platinum cage, which is heated to $\approx 1600^\circ\text{C}$ by a modified Lindberg furnace. The resulting CO_2 is measured volumetrically. The coefficient of variation for the determination of C in a tungsten carbide sample is 0.033 per cent. of C.

A. R. ROGERS

104. Volumetric analysis by the use of chromous salts. XII. Potentiometric titration of tungsten with chromous sulphate. Isao Muraki (*J. Chem. Soc. Japan, Pure Chem. Sect.*, 1955, 76 [2], 193-196).—Acidic soln. (> 6 N HCl) of WO_4^{2-} are quant. reduced at room temp. by 0.1 N CrSO_4 soln. (obtained by the reduction of Cr^{+++} with zinc amalgam) to produce W^{IV} . The change in e.m.f. (vs. the S.C.E.) is 0.15 V and the titration can be

carried out potentiometrically with a platinum electrode. The presence of PO_4^{3-} , F^- or citrate makes the change in potential less distinct. Ferric ions do not affect the reduction of WO_4^{2-} by Cr^{++} , and both Fe^{+++} and WO_4^{2-} are differentially titrated with CrSO_4 in conc. HCl soln. XIII. Potentiometric titration of persulphate with chromous sulphate. Isao Muraki (*Ibid.*, 1955, 76 [2], 196-198).—Persulphate ions are reduced by Cr^{++} in 1.8 N H_2SO_4 to give SO_4^{2-} and Cr^{+++} . The change in the e.m.f. is ≈ 0.5 V and a potentiometric titration of $\text{S}_2\text{O}_8^{2-}$ is effected by the use of a platinum electrode, with an error of $< \pm 0.2$ per cent. No interference results from the presence of large amounts of K^+ and SO_4^{2-} . XIV. Potentiometric titration of selenous acid with chromous sulphate. Isao Muraki (*Ibid.*, 1955, 76 [2], 198-201).—Selenous ions are quant. reduced with 0.1 N CrSO_4 soln. in 1 to 5 N HCl or H_2SO_4 . The addition of NaCl results in a quicker coagulation of colloidal Se. The potentiometric titration, with a platinum electrode, provides good results. The attempt to titrate differentially both Fe^{+++} and SeO_3^{2-} with CrSO_4 met with little success, even in the presence of tartrate, F^- or PO_4^{3-} . XV. Potentiometric titration of ferriyanide and vanadate with chromous sulphate. Isao Muraki (*Ibid.*, 1955, 76 [2], 201-203).—The potentiometric titration of $\text{Fe}(\text{CN})_6^{3-}$ with Cr^{++} in HCl (1 to 5 N) is affected by Zn^{++} which are likely to be present in the Cr^{++} soln. A known excess of 0.1 N CrSO_4 is added to $\text{Fe}(\text{CN})_6^{3-}$ soln. in N HCl and titrated with 0.04 N methylene blue soln. Vanadate is quant. reduced to VO_2^+ by Cr^{++} in dil. HCl (1 to 2.5 N) or H_2SO_4 (2.5 to 9 N). The change in the e.m.f. at the end-point is ≈ 0.3 V. In the presence of iodine chloride (0.005 M, 3 ml) VO_2^+ are successively reduced to V^{+++} in the same soln. by Cr^{++} , involving a change in potential of 0.5 V. K. SAITO

105. The paper-chromatographic separation of uranium (VI). G. Almássy and M. Vígvári (*Magyar Kém. Foly.*, 1955, 61 [4], 109-111).—By varying the pH of the solvent, optimum conditions were found for the ascending paper-chromatographic separation of $< 3 \mu\text{g}$ of U^{VI} . The solvent is ether-ethanol-conc. HNO_3 (70:23:7), giving an R_F value of 0.84 on Macherey Nagel 214 paper pre-saturated with vapour. Ferric iron gives R_F 0.14, other metals even lower values. The spot is detected with 5 per cent. aq. $\text{K}_4\text{Fe}(\text{CN})_6$. By comparing the size and the colour of the spot with a standard sample, the content of U^{VI} ($< 5 \mu\text{g}$ in 0.1 ml) can be estimated with ± 30 per cent. accuracy. If Fe^{III} is absent, the R_F is < 0.84 , thus $100 \mu\text{g}$ of Fe^{III} are added to the spot on the paper, if necessary. A slightly modified, simple and rapid (10 to 15 min.) qual. method is also described for quantities of $< 1 \mu\text{g}$. A. G. PETO

106. Volumetric estimation of uranium. I. With potassium dichromate, with N-phenylanthranilic acid as internal indicator. V. Panduranga Rao, B. V. S. R. Murty and G. Gopala Rao (Andhra Univ., Visakhapatnam, India) (*Z. anal. Chem.*, 1955, 147 [2], 99-105).—With N-phenylanthranilic acid as internal indicator, salts of U^{IV} in H_2SO_4 soln. (> 2 N) can be titrated against $\text{K}_2\text{Cr}_2\text{O}_7$ soln. at room temp. Procedure.—To 10 to 25 ml of a 0.05 N soln. of a salt of U^{IV} add 50 ml of 10 N H_2SO_4 soln. and dilute to 100 ml. Add 2 drops of N-phenylanthranilic acid soln. (0.1 g dissolved in an equivalent quantity of Na_2CO_3 soln. and diluted to 100 ml) and titrate with 0.05 N $\text{K}_2\text{Cr}_2\text{O}_7$ until the

colour of the oxidised indicator is visible. **II. With sodium vanadate as reagent.** V. Panduranga Rao, B. V. S. R. Murty and G. Gopala Rao (*Ibid.*, 1955, 147 [3], 161-173).—It is shown that the difficulty experienced in the titration of U^{IV} with vanadate at room temp., with diphenylbenzidine (I) or N-phenylanthranilic acid (II) as indicator, is due to the slowness of the reversible oxidation and reduction of the indicators. The catalysis of the reactions has been studied, and three methods are given for the rapid determination of U^{IV} at room temp. The results are accurate to ± 0.1 per cent. **Procedure**—(i) Mix the sample (10 to 25 ml, ≈ 0.05 N) with 10 N H_2SO_4 (10 ml), M oxalic acid (2 ml), syrupy phosphoric acid (5 ml) and 0.1 per cent. I (0.5 ml), dilute to 100 ml and titrate with standard sodium vanadate. (ii) Mix the sample with 10 N H_2SO_4 (50 ml) and 0.1 per cent. II (2 drops), dilute to 100 ml and titrate. (iii) Mix the sample with 10 N H_2SO_4 (40 ml), M oxalic acid (2 ml) and 0.1 per cent. II (2 drops), dilute to 100 ml and titrate. A. R. ROGERS

107. The determination of halide ions by electrophoresis. Eiichi Ohara and Hideo Nagai (*J. Chem. Soc. Japan, Pure Chem. Sect.*, 1955, 76 [3], 291-294).—The electrophoretic distribution of Cl⁻, Br⁻ and I⁻ (potassium salts) was studied in dil. lactic acid (at 300 V). The mobilities of these three anions decrease in the sequence Br, I, Cl in acid of concn. < 0.5 M, and I, Br, Cl in a more concentrated soln. of lactic acid, and have different values from those obtained by ordinary paper-chromatography. The chromatographic migration of these ions appears to compete with the electrolyte migration. The application of a potential does not necessarily result in a better separation of the spots. K. SAITO

108. Spectrophotometric determination of fluoride. E. D. Schall and H. G. Williamson (Purdue Univ., Lafayette, Ind., U.S.A.) (*J. Ass. Off. Agric. Chem.*, 1955, 38 [2], 454-459).—The method is based on the interference of F⁻ with the development of a coloured complex between titanium and ascorbic acid (Hines and Boltz, *Brit. Abstr. C*, 1952, 478). The sample (1 g) is moistened with satd. aq. magnesium acetate soln. (5 ml); dried and ignited in a nickel crucible at 600°C for 2 hr. By using 25 to 30 ml of 60 per cent. $HClO_4$ the ash is transferred to a flask, chloride is pptd. with solid Ag_2CO_3 , and the fluoride is distilled at 140°C; 190 ml of distillate are collected and diluted to 200 ml. Of this an aliquot part (≈ 5 mg of fluoride) is treated with 10 ml of titanium reagent (10 g of potassium titanium oxalate per litre), 25 ml of buffer (30.6 g of K H phthalate and 26.2 ml of N NaOH diluted with water to 1 litre) and 10 ml of ascorbic acid reagent (6.50 g of L-ascorbic acid and 5 g of $NaHSO_4$ dissolved in water to 500 ml). The mixture is diluted to 100 ml and the absorbance is determined in a Beckman model DU spectrophotometer against standard fluoride solution (1 g per litre). The results are calculated from the curve constructed from determinations on standard solutions. The method detects ≈ 1 p.p.m. of fluoride. A. A. ELDRIDGE

109. Overcoming the effect of manganese dioxide in fluoride determinations. S. Deutsch (Kaiser Steel Corp., Fontana, Calif., U.S.A.) (*Anal. Chem.*, 1955, 27 [7], 1154-1155).—Micro-determinations of fluoride in plant tissue by the modified Willard-Winter method (Remmert and Parks, *Brit. Abstr. C*, 1953, 324) are often hampered by a fading end-point during the titration with $Th(NO_3)_4$ soln. This is

due to bleaching of the alizarin red S indicator by Cl⁻ liberated from MnO_2 and chlorides present in the plant tissue. The addition of 3 per cent. H_2O_2 to the flask before the start of distillation eliminates this interference without affecting the fluoride recovery or subsequent titration. A. R. ROGERS

110. Qualitative and quantitative determination of chlorates with the aid of phenylanthranilic acid. N. A. Bil'yk (*Tr. Odessk. Un-ta, Sb. Khim. Fak.*, 1953, 3, 127-131; *Referativnyi Zh., Khim.*, 1955, Abstr. No. 7,673).—To detect ClO_3^- , 1 ml of test soln. is mixed in a test-tube with 0.1 ml of a 0.1 per cent. alkaline soln. of phenylanthranilic acid, and 0.1 to 2 ml of conc. H_2SO_4 or conc. HCl are poured down the side of the tube; a violet-crimson colour at the surface of the H_2SO_4 , or a pink-crimson colour at the surface of the HCl, indicates the presence of ClO_3^- . With H_2SO_4 , the limiting concn. is 1 in 10^6 and the sensitivity limit is $1 \mu g$. The colour is not extracted by organic solvents. The reaction can be used for the quantitative colorimetric determination of ClO_3^- in concn. of < 0.005 mg per ml; the relative error is 1.8 per cent. Ions of K, Na, NH_4 , Mg, Ca and Sr do not interfere, but oxidising agents must be absent; Bi^{3+} and NO_3^- interfere when HCl is used. E. HAYES

111. Determination of small amounts of chlorate in ammonium perchlorate. C. Eger (Ministry of Defence, Tel-Aviv, Israel) (*Anal. Chem.*, 1955, 27 [7], 1199-1200).—A method is described for the determination of < 0.1 per cent. of ammonium chlorate in ammonium perchlorate, based on a colour reaction with brucine. Periodate, nitrate, Fe^{3+} (> 0.005 per cent.) and IO_3^- (> 0.033 per cent.) interfere. **Procedure**—Dissolve the sample (10 g) in H_2O (100 ml) and filter. Mix an aliquot (1 to 5 ml) with ice-cold 32 per cent. H_2SO_4 (10 ml) and 5 per cent. brucine in glacial acetic acid (0.5 ml). Heat in a boiling-water bath for 15 min., cool with ice, dilute with H_2O to 25 ml, and compare the extinction at 435 m μ in 2-cm cells with a reagent blank. Calculate the concn. of chlorate by means of a calibration curve. A. R. ROGERS

112. Volumetric determination of manganese after oxidation to the quadrivalent state stabilised by tellurate. I. M. Issa and I. F. Hewaidy (Univ. Cairo, Giza, Egypt) (*Chemist Analyst*, 1955, 44 [3], 70-71).—The procedure makes use of an oxidation of Mn^{II} to the quadrivalent state by alkaline H_2O_2 , in the presence of telluric acid, and a subsequent titration with oxalic acid or Fe^{2+} in acid medium. The sample solution should contain from 3 to 55 mg of Mn and should be about 0.1 N in acid. For every 5 mg of Mn, 0.08 g of telluric acid is added and stirred until dissolved. Then 5 M NaOH is added until the solution is 2.5 M with respect to NaOH. About 0.2 ml of 20-vol. H_2O_2 is added for each 5 mg of Mn and the solution is stirred until it becomes clear and reddish. Excess of H_2O_2 is decomposed by heating, and to the hot solution a measured excess of 0.1 N oxalic acid solution and then an excess of 2 M H_2SO_4 are added. Excess of oxalic acid is titrated at 60° to 80° C with 0.1 N $KMnO_4$. Alternatively, the solution is cooled and acidified with 2 M H_2SO_4 , before adding a measured excess of 0.1 N $FeSO_4$ and back-titrating with $KMnO_4$ soln. If A be the vol. (ml) of reducing agent added, B the vol. (ml) of $KMnO_4$ soln. used of normality N, and C the vol. (ml) of $KMnO_4$ soln. equivalent to A, then mg of Mn = $2.747 N(C-B)$. O. M. WHITTON

113. Compleximetric determination of manganese in spiegeleisen and other ferromanganese alloys. H. Flaschka and R. Püschel (Tech. Univ. Graz, Austria) (*Chemist Analyst*, 1955, **44** [3], 71-73).—The two procedures described exemplify the use of Tiron (disodium catechol-3;5-disulphonate) and cyanide as masking agents, e.g., for Fe, Ti and Al, in the analysis of manganese alloys with EDTA. The applicability and limitations of these procedures are discussed. O. M. WHITTON

114. Flame-spectrophotometric determination of iron in siliceous materials. J. A. Dean and J. C. Burger, jun. (Univ. Chem. Dept., Knoxville, Tenn., U.S.A.) (*Anal. Chem.*, 1955, **27** [7], 1052-1055).—The Beckman model DU flame spectrophotometer with an oxy-acetylene flame has been applied to the rapid determination of Fe in siliceous materials such as alumina refractories and limestone. The sample is prepared by ignition with HF and H_2SO_4 , then dissolved in dil. HCl. The arc emission line at 2860 Å is used for measuring the Fe radiation. Interference from most other elements is corrected by the internal-standard technique (Co 3871-Å line), but Mg must be eliminated by a preliminary separation of the Fe as hydrated ferric oxide. The optimum concn. range for Fe is 25 to 200 p.p.m. The standard deviation from the mean of replicate samples is ≈ 3 per cent. A. R. ROGERS

115. A new colorimetric determination of ferrous iron with *m*-methoxy-*o*-nitrosophenol. Tetsuya Torii (*J. Chem. Soc. Japan, Pure Chem. Sect.*, 1955, **76** [3], 333-336).—The ferrous complex of *m*-methoxy-*o*-nitrosophenol (I) is not extracted with organic solvent from an aq. soln. of pH 2.0 to 10.0. The sample soln. is treated with acetate buffer (pH 3.8) (5 ml) and a saturated aq. soln. of I (5 ml). The excess of I is removed by shaking with CCl_4 (5 ml). The aq. layer is made up to 25 ml and the extinction is measured at 700 $m\mu$, and is in accord with Beer's law up to 1.0 μg per ml. No interference results from the presence of metal ions except Cu^{++} , which can be masked with $Na_2S_2O_3$. This method appears to be suitable for the determination of Fe^{++} in water. Ferric ions can be determined similarly, after reduction to Fe^{++} with hydroxylamine. K. SAITO

116. Ascorbic acid solutions in volumetric analysis. I. Differential and potentiometric titration of trivalent iron, bivalent copper and vanadate. Chozo Yoshimura and Takumi Fuzitani (*J. Chem. Soc. Japan, Pure Chem. Sect.*, 1955, **76** [3], 304-306).—The differential titration of binary and tertiary mixtures of Fe^{+++} , Cu^{++} and VO_4^{3-} was studied by the use of standard ascorbic acid soln. (0.1 N). The amounts of (Fe + V), (Fe + Cu), (Cu + V) and (Fe + Cu + V) can be determined by adding a large excess of KI to the acidic soln. of the sample and titrating the liberated iodine with ascorbic acid. The acidity of the soln. must be adjusted to a pH of 5 to 6 by adding $NaHCO_3$ before the titration is started. Ferric ions can be masked by the addition of NH_4F . Vanadate can be directly titrated with ascorbic acid, diphenylamine being used as indicator. By using a platinum-tungsten electrode, ($Fe^{+++} + VO_4^{3-}$) can be directly titrated with ascorbic acid soln. in 0.1 to 0.5 N HCl. K. SAITO

117. 4-Dimethylamino-2:3-dimethyl-1-phenylpyrazol-5-one [amidopyrine] for detection of the ferricyanide ion. N. E. Pérez Roura (Univ. Nacl. Córdoba, Arg.) (*Rev. Asoc. Bioquím. Argentina*, 1954,

19, 225-226).—A mixture of 5 ml of ferricyanide soln. heated with 1 ml of 5 per cent. amidopyrine in 2 N HCl gives a green colour. The ether extract shows a Nile-blue fluorescence in u.v. light and a lilac one in direct light. The fluorescence is stable for more than 24 hr. Ferrocyanide gives a blue colour and shows no fluorescence in ether soln. CHEM. ABSTR.

118. A new colorimetric determination of cobalt with *m*-methoxy-*o*-nitrosophenol. Tetsuya Torii (*J. Chem. Soc. Japan, Pure Chem. Sect.*, 1955, **76** [3], 328-333).—*m*-Methoxy-*o*-nitrosophenol (I) was synthesised by nitrosating monomethylresorcinol. I is soluble in CCl_4 and benzene, the CCl_4 soln. having max. absorption at 325 $m\mu$. Cobalt (5 to 50 μg) is treated with 30 per cent. H_2O_2 (2 to 3 drops), ammonium citrate (40 per cent., 1 ml) (to mask Fe) and a saturated aq. soln. of I (5 ml). The pH is adjusted to between 7 and 8.5 with aq. NH_3 soln. and the aq. layer is extracted with CCl_4 (≈ 10 ml, in several portions). The excess of I is removed by shaking with Na_2CO_3 soln. (10 per cent., 10 ml), and the extinction of the CCl_4 layer is measured at 400 $m\mu$. No other metal complex of I is extracted with CCl_4 under the given conditions. The CCl_4 soln. of the cobalt complex conforms to Beer's law within the range 0.02 to 2.5 μg per ml. This method can be used in the presence of Ni (< 1000 times the weight of the Co), Fe^{++} (< 1000 times), Fe^{+++} (< 5000 times), and Cu^{++} (< 2 times). Higher concn. of Cu^{++} must be masked with $Na_2S_2O_3$, which does not affect the determination of Co. The average deviation from the mean is < 5 per cent. K. SAITO

119. Spectrophotometric determination of nickel in tungsten powder. K. L. Rohrer (Sylvania Electric Products Inc., Towanda, Pa., U.S.A.) (*Anal. Chem.*, 1955, **27** [7], 1200-1203).—The method of Alexander, Godar and Linde (*Brit. Abstr. C*, 1946, 155) for the determination of Ni has been applied to the estimation of 1 to 50 μg of Ni in tungsten powder with an average deviation < 1 μg . The Ni is separated by a $CHCl_3$ extraction of Ni^{II} -dimethylglyoxime complex in the presence of the H_2O_2 used to dissolve the sample, and determined spectrophotometrically (385 $m\mu$) as the diethyl-dithiocarbamate complex. The addition of hydroxylamine hydrochloride is necessary to effect complete recovery, and ammonium citrate soln. of the complexing reagents should be used to prevent interference from Fe. A. R. ROGERS

120. Semi-quantitative analysis of a small amount of metal by paper chromatography. I. Nickel in cobalt salts. Shirō Harasawa and Kunihiro Takasu (*J. Chem. Soc. Japan, Pure Chem. Sect.*, 1955, **76** [2], 173-176).—One drop of the sample soln. (> 0.003 mg of Ni per ml) is developed with acetone containing 5 per cent. v/v conc. HCl and revealed with rubenic acid. The mobility of Ni^{++} is little affected by the presence of a large amount of Co (< 3000 times the weight of Ni) so that a paper-chromatographic detection of a micro amount of Ni in Co can be effected. The area of the spot of Ni is almost independent of concn., but the intensity of coloration decreases with the decrease of Ni. When the colour of the spot is compared with that of standard samples, an approximate estimation of Ni can be effected. K. SAITO

121. Spectrophotometric determination of ruthenium. G. A. Stoner (Dow Chem. Co., Midland, Mich., U.S.A.) (*Anal. Chem.*, 1955, **27** [7], 1186-1187).—A method is described for the determination

of 0.1 to 12 mg of Ru by measuring the extinction of potassium perruthenate in alkaline soln. at 380 m μ . The only interfering element (Os) is removed as tetroxide by preliminary distillation with HNO₃. To the residue add H₂SO₄, evaporate to fuming, cool and add conc. HCl (5 drops), phosphoric acid (1 ml), sodium bismuthate (1 g) and 70 per cent. perchloric acid (10 ml). Distil for 30 min. in an all-glass apparatus, passing a stream of air and collecting the distillate in 2 M KOH (50 ml). Dilute with H₂O to 100 ml and, after 30 min., measure the extinction at 380 m μ in 1-cm cells. Calculate the concn. of Ru from a standard curve.

A. R. ROGERS

122. The chemical analysis of inorganic micro-constituents. I. Analysis of micro quantities of palladium by catalytic formation of molybdenum blue. Takanobu Shiokawa, Tomihisa Kambara and Masuo Yagi (Shizuoka Univ., Japan) (*Japan Analyst*, 1955, **4** [4], 224-227).—The reduction of MoO₄²⁻ with H₂PO₄⁻ in dil. HCl (\approx 1 N) is catalysed by traces of Pd²⁺. For the detection of Pd, one drop (0.05 ml) of the sample soln. is mixed with one drop each of (NH₄)₂MoO₄ (4 per cent.) and NaH₂PO₄·H₂O (20 per cent.). The time taken for the production of the blue colour is compared with a blank test with N HCl (limit of detection 0.05 μ g, limit of concn. 1 in 11 \times 10⁶). When the rate of colour formation is measured by means of an electro-photometer at 24°C, a micro amount of Pd (4 to 11 μ g per ml) can be determined. Interference results from the presence of Hg²⁺ (> 10 μ g per ml), SCN⁻ (> 10 μ g), Fe²⁺ (> 20 μ g), Ni (> 20 μ g), Co (> 300 μ g) and Pt (> 100 μ g). **II. Analysis of micro quantities of palladium by catalytic formation of tungsten blue.** Takanobu Shiokawa, Tomihisa Kambara and Masuo Yagi (*Ibid.*, 1955, **4** [4], 227-230).—The rate of formation of tungsten blue in dil. HCl from tungstophosphate and hypophosphite is catalysed by a micro amount of Pd. For the detection of Pd one drop of the sample soln. is mixed with one drop each of tungstophosphoric acid (4 per cent.) and NaH₂PO₄·H₂O soln. (20 per cent.) (limit of detection 0.11 μ g, limit of concn. 1 in 4.5 \times 10⁴). Tungstosilicic acid can be used in place of tungstophosphoric acid (limit of detection 0.06 μ g). By measuring the rate of the reduction of WO₄²⁻, Pd (10 to 50 μ g per ml with tungstophosphoric acid, 3 to 7 μ g with tungstosilicic acid) can be determined in the absence of Pt, Fe, Co, Ni and Cu.

K. SAITO

123. Rapid analysis of ash from coal and oil shale by colorimetric methods. N. N. Bannerjee and B. A. Colliss (*Fuel, Lond.*, 1955, **34**, April Suppl., s71-s83).—Colorimetric methods for the determination of SiO₂, Al₂O₃, Fe, Ti, Mn, Mg, Ca, P, Ge and V in coal and oil shale are described. The time required for the analysis is > 2 days. Four solutions of the ash are prepared in which the various constituents are determined by known methods.

N. E.

124. Direct estimation of the mineral content of coal. W. Radmacher and P. Mohrhauer (*Brennstoff-Chemie*, 1955, **36** [15-16], 236-239).—The direct estimation of the mineral content of coal is effected by determining the loss in wt. caused by treating the coal with HCl and with HF; determining the content of ash, Cl and Fe in the treated coal; calculating the amount of pyrites from the amount of Fe found; and using the formula, mineral content

$$= \frac{(G_1 - G_2) + P + C + A}{G_1} \times 100, \text{ where } G_1 \text{ is}$$

the wt. (g) of the dried coal sample, G_2 is the wt. (g) of the coal after the acid treatment and after drying, P is the wt. (g) of the pyrites present in the coal sample, C is the amount of Cl (g) in the treated coal (found by determination), and A is the wt. (g) of the iron oxide in the ash of the treated coal. The analyses of a number of coals are described and the results are compared with those obtained by methods using the King, Maries and Crossley (KMC) formula. The method is suitable for use in series analysis.

H. L. WHITEHEAD

125. Spectrochemical analysis of silicate rocks by means of rotating logarithmic sector method. Hiroshi Hamaguchi and Rokuro Kuroda (Tokyo Univ. Educ.) (*Japan Analyst*, 1955, **4** [4], 207-210).—A rapid spectrochemical determination of Ni, Co (both 0.0005 to 0.1 per cent.), Sn (0.003 to 0.1), Pb (0.001 to 0.1) and Ge (0.001 to 0.1) was studied with the aid of a rotating logarithmic sector. To stabilise the light source, the sample is mixed (2:1) with NaCl containing 2.92 per cent. of Bi₂O₃ as the internal standard and burnt in a carbon arc (170 V, d.c., 7 amp., exposure 45 sec.). No appreciable differential evaporation of the elements is observed within the period of exposure. The spectral lines are recorded on a photographic plate and the lengths are compared with those of Bi (2989.03 and 3397.21 Å). The standard samples are prepared by mixing known amounts of the elements with a silicate cake (Al₂O₃, 30; SiO₂, 55; and Na₂CO₃, 15 per cent.) (for Ni and Co), or with powdered basalt that is free from Pb, Sn and Ge. K. SAITO

126. Studies on the oxy-acid phosphors. IV. Application of polarography to the determination of activators, especially in calcium silicate phosphors. Yoshihide Kotera (*Rep. Gov. Chem. Ind. Res. Inst., Tokyo*, 1955, **50** [2], 47-51).—The determination of small amounts of activators in phosphors was studied by polarography, and the relationship between the concn. of activator and the brightness of the phosphor is discussed. Manganese (0.5 to 10 per cent.) in Zn₂SiO₄ or in (Zn,Be)₂SiO₄ is determined by dissolving the samples in 6 N HCl and recording the polarographic wave of Mn (E_1 , -1.3 V vs. the S.C.E.) in an ammoniacal soln. containing KCN. Calcium phosphate phosphors are fused with Na₂CO₃ (8 times the weight of the sample), dissolved in HCl to give a 3 N soln. and submitted to polarography to determine the contents of Mn (1 to 5 per cent.) and Sb (0.5 to 2 per cent.). Calcium silicate phosphors are heated with HCl repeatedly until no luminescence can be observed on the residue, which is extracted with water, filtered and made acid with HCl to give a 3 N soln. Lead (0.02 to 0.3 per cent.) is determined polarographically in this soln. For the determination of Mn (\approx 0.5 per cent.), the HCl soln. is made ammoniacal and submitted to polarography.

K. SAITO

See also Abstracts 1, 7, 153, 154, 155, 277, 289, 290, 291, 312.

3.—ORGANIC ANALYSIS

127. Organic spot analysis. F. Feigl (Min. Agric., Rio de Janeiro, Brazil) (*Anal. Chem.*, 1955, **27** [8], 1315-1318).—The use of organic preparative procedures as the bases of qual. micro-analytical tests for organic compounds or functional groups is discussed. Methods for the detection of phenols, acyl derivatives of aromatic amines, arylurethanes and

monoaryureas, and sulphonic acids are described. Phenols are detected by their reaction with sodium cobaltinitrite in acetic acid soln., and give a brown to yellow colour or brown ppt.; quantities of 0.5 to 20 μg were detected with the phenols investigated. Acyl derivatives of aromatic amines, arylurethanes and monoaryureas are detected by nitrosation followed by treatment with 1-naphthol. A red or orange colour appears on warming; the limit of detection is between 0.1 and 5 μg , according to the derivative tested. Sulphonic acids are detected by the formation of NaHSO_3 when heated with alkaline Na formate, the HSO_3^- being treated with ferri-ferricyanide soln. to form Prussian blue; 0.25 to 5 μg were detected. The Vieboeck-Zeisel procedure for the quant. determination of methoxy and ethoxy groups provides the basis of a sensitive test for organically bound I; 0.05 to 1 μg can be detected.

G. P. COOK

128. Polarographic determination of sulphur in organic compounds. As. Trifonov, Ch. Ivanov and D. Pavlov (Lehrstuhl Chemie, Sofia) (*Compt. Rend. Acad. Bulg. Sci.*, 1954, **7** [1], 1-4).—The sample containing 0.015 to 2.5 mg of S is treated with Raney Ni in H_2O , ethanol or benzene by shaking for 10 min. Refluxing is required for oxygenated compounds of S. The H_2S formed on the addition of H_2SO_4 is distilled with H into 0.1 N NaOH. The S^{2-} can be polarographed directly or the increase in the cadmium wave can be measured. In either case an aliquot containing 0.05 to 0.1 mg of S is used. All organic and inorganic types of S can be determined. The presence of N or halogens has no effect. Pure S can be used to construct the calibration curve.

CHEM. ABSTR.

129. Separation of alcohols as their alkyl hydrogen phthalates by partition chromatography. R. E. Henze (Purdue Univ., Lafayette, Ind., U.S.A.) (*Anal. Chem.*, 1955, **27** [8], 1349-1351).—A direct visual method of partition chromatography on silica gel for separating derivatives of the normal aliphatic alcohols (C_1 to C_6) from a multi-component mixture is described. The alcohols are treated with phthalic anhydride and the hydrogen phthalate esters are extracted into CHCl_3 from acid soln., after removal of excess of anhydride, unchanged alcohols and diesters by extraction with benzene. The hydrogen phthalate esters are separated on silicic acid columns, the composition and the eluting agent used being dependent on the type of ester. Identification of the bands is accomplished by comparison with the position of known esters run alone on an identical column and developed to the same degree. The method was used in the separation and identification of components of the volatile substances produced by stored apples.

G. P. COOK

130. Paper chromatography of sugar alcohols and their glycosides. J. Cerbulis (S. F. Whitman and Son Inc., Philadelphia, U.S.A.) (*Anal. Chem.*, 1955, **27** [9], 1400-1401).—Sugar alcohols and their glycosides are detected by treatment with *p*-anisidine after paper-chromatographic separation, a mixture of *n*-propanol, ethyl acetate and water being used as solvent. The filter-paper is sprayed with the reagent, and heated at 100°C for 10 to 15 min.; the sugar alcohols and glycosides leave white spots on a pale-brown background. The R_F values for 19 polyols are listed. G. P. COOK

131. A new spot test for formaldehyde. P. W. West and B. Sen (Louisiana State Univ., Baton Rouge, La., U.S.A.) (*Anal. Chem.*, 1955, **27** [9],

1460-1461).—Test papers for formaldehyde are prepared by impregnating filter-paper with an equilibrium mixture of potassium tetracyanonickelate and dimethylglyoxime. On addition of formaldehyde the CN^- is removed through the formation of cyanohydrin, with subsequent liberation of Ni^{2+} and formation of the red Ni dimethylglyoximate. As little as 0.5 μg can be detected and semi-quantitative results can be obtained by matching the colour against standard papers. No interference from more than 40 common organic compounds tested was found.

G. P. COOK

132. Determination of carboxylic acid anhydrides by reaction with morpholine. J. B. Johnson and G. L. Funk (Carbide and Carbon Chem. Co., S. Charleston, W. Va., U.S.A.) (*Anal. Chem.*, 1955, **27** [9], 1464-1465).—The method, which enables the determination of anhydride independent of the possible acid content of the sample, is based on the reaction of the anhydride with morpholine and titration of the excess of reagent with standard HCl in methanol soln. to a methyl yellow-methylene blue indicator. On application to eight different anhydrides, results within ± 0.2 per cent. were obtained; good results were also obtained with low concn. of acetic anhydride in glacial acetic acid.

G. P. COOK

133. Analysis of reaction products by isotope-dilution procedure. Examination of acrylic acid-ethyl alcohol reaction mixtures for diethyl ether formation. G. Burtle and J. P. Ryan (Minn. Mining and Manf. Co., St. Paul, Minn., U.S.A.) (*Anal. Chem.*, 1955, **27** [8], 1215-1217).—An isotopic dilution procedure in which ^{14}C -labelled ether is used as tracer has been used to determine the amount of by-product ether produced in the esterification of ethanol with acrylic acid. The method was found to be highly sensitive and revealed small but definite amounts of ether in reaction mixtures with different catalysts, whereas other methods of analysis (including i.r.) had failed to indicate its presence.

K. A. PROCTOR

134. The micro-detection and colorimetric micro-determination of the oxalate ion by means of an activated reaction. G. Almássy and I. Dezső (*Magyar Kém. Foly.*, 1955, **61** [4], 107-109).—Numerous oxidation-reduction reactions that are catalysed by oxalate ions and are accompanied by colour change were examined. For qual. testing, the V^{V} -aniline reaction was used; the quant. method is based on the oxidation, by Cr^{VI} , in the presence of oxalate ions and in H_3PO_4 soln., of Mn^{II} to Mn^{III} oxalate. On being boiled, Mn^{III} is reduced to Mn^{II} and CO_2 is evolved; this process is repeated as long as oxalate is present. The excess of Cr^{VI} is determined by the diphenylcarbazide method (*Anal. Chem.*, 1952, **24**, 1016). *Procedure*—To 1 ml of an oxalate soln., containing > 0.1 N mineral acid, add 5 drops of N HCl, 3 drops of a charcoal-treated and filtered soln. of 10 ml of aniline oil in 40 ml of conc. HCl and 50 ml of H_2O , and add also 3 drops of 0.1 N V^{V} soln. (9.1 g of V_2O_5 dissolved in a soln. of 25 g of NaOH in 100 ml of H_2O , acidified with 75 ml of conc. HNO_3 and diluted to 1 litre with H_2O). In the presence of oxalate, a greenish-blue colour, and later a ppt., appears. The detection of 1 μg of oxalate ion in a 1-ml sample is possible. A blank test gives a greenish-yellow colour. With 1 μg , the colour appears in 5 to 10 min. Most metals do not interfere; neither does Co^{II} , Ni^{II} , Cr^{III} or Cu^{II} in 1-mg quantities. The presence of many foreign ions decreases the reaction velocity. For

quant. estimation, dilute a Na oxalate solution (0.5 to 10 ml, containing 10 μ g of oxalate per ml) to 10 ml; add conc. H_3PO_4 (0.5 ml), 10 per cent. $Na_2CO_3 \cdot H_2O$ (1 ml), and 1 ml of Mn^{II} soln. containing 1000 μ g, and 0.02 per cent. $K_2Cr_2O_7$ (0.5 ml). Heat at 100° C for 10 min., add diphenylcarbazide reagent (2 ml), dilute to 50 ml and determine photometrically after 5 min. (S53 filter). Distilled water is used as a blank. The Beer - Lambert law is not obeyed. Limiting concentrations are 0.5 to 10 μ g of oxalate per ml; $> 5 \mu$ g of oxalate are needed. Optimum conditions and effect of other ions have been studied.

A. G. PETO

135. Paper-chromatographic examination of some organic acids, with special reference to oxalic acid. T. Perlusz and K. Jeney (Tobacco Res. Inst., Budapest) (*Magyar Kém. Foly.*, 1955, **61** [1], 13-17).—Oxalic, citric, tartaric, malic, fumaric, maleic, succinic, lactic and adipic acids can be separated by this method. For ascending chromatography in alkaline medium (Schleicher and Schüll 597 paper), samples containing 0.32 to 5.0 per cent. of acids were run in 96 per cent. ethanol - conc. aq. NH_3 (80:16:4, by vol.). For spraying, a mixture (1:1) of the sodium salt of methyl red (0.2 per cent. in ethanol) and methylene blue (0.1 per cent. in ethanol) was used. Maleic and succinic acids cannot be separated by this method. In an alternative method, the filter-paper was impregnated with 0.1 N HCl and dried at room temp. Samples of 2 μ l were used, containing 0.32 to 5.0 per cent. of organic acid. These were developed with *n*-butanol-xylene (1:1) saturated with 0.1 N HCl. The completed chromatogram was immediately dried at 92° C for 3 hr. and then sprayed with bromophenol blue (0.4 per cent.) in 96 per cent. ethanol, containing 4 ml of Michaelis acetate buffer (pH 5) for each original 100 ml of the soln. For quant. estimation 2 μ l of the soln. were used on a paper prepared as above, and then sprayed with bromophenol blue; the size of the spots was measured with a planimeter. The calibration curve was obtained similarly by the method of the least squares. The equation, $area = k \times \log \text{concn.} + b$, is obeyed. The probable error, using Schleicher and Schüll 2043 paper, is 6.7 to 14.6 per cent., according to the acid. Lists of R_F values are given.

A. G. PETO

136. A new method for the micro-determination of citric acid. H. Boser (*Naturwissenschaften*, 1955, **42** [15], 440).—The method is based on the formation of a soluble copper complex by citric acid. Under the conditions of amino-acid analysis (Pope and Stevens) (using copper phosphate suspension), the complex has the composition 1 atom of Cu: 1 mol. of citric acid over a wide range of concentrations. Paper chromatograms can be obtained from which the citrate zone is cut and treated with copper phosphate suspension. The copper in the filtrate is determined with Na diethyldithiocarbamate. The method is suitable even for very complicated mixtures if the solvent used for the chromatography is ethanol - aq. NH_3 (0.88) - water (80:4:16).

S. R. NEUBERGER

137. Spectrophotometric determination of esters and anhydrides by hydroxamic acid reaction. R. F. Goddu, N. F. LeBlanc and C. M. Wright (Hercules Powder Co., Wilmington, Del., U.S.A.) (*Anal. Chem.*, 1955, **27** [8], 1251-1255).—The method is based on the formation of hydroxamic acids by the interaction of esters and anhydrides, in alkaline soln., with hydroxylamine. The hydroxamic acids form highly coloured chelate complexes with Fe^{+++} ,

which give absorption maxima at 530 $m\mu$ for aliphatic, and broad max. at 550 to 560 $m\mu$ for aromatic, esters. Molar absorption coefficients and wavelengths for 20 different esters are listed and methods are given for the determination of esters, and lactones or anhydrides in the presence of esters. For esters or anhydrides alone the precision and accuracy are within ± 2 per cent., but for mixtures of the two the results are less accurate. The optimum concn. range is 10^{-3} to 10^{-2} M, and acids, most amides and nitriles do not interfere. High concn. of carbonyls, Cu, Ni or V, and ions or compounds that complex Fe^{+++} may affect the colour intensity.

G. P. COOK

138. Identification of amines from X-ray powder diffraction diagrams of their hydrochloride derivatives. M. J. Brock and M. J. Hannum (Firestone Tire and Rubber Co., Akron, Ohio, U.S.A.) (*Anal. Chem.*, 1955, **27** [9], 1374-1378).—A simple procedure is described for the identification of milligram quantities of amines by studying the X-ray powder diffraction diagrams of their hydrochlorides. The preparation of the derivatives and X-ray specimens is described and diffraction data are tabulated for 52 aliphatic and aromatic amines. K. A. PROCTOR

139. Use of 1:2-naphthaquinone-4-sulphonate for the estimation of ethyleneimine and primary amines. D. H. Rosenblatt, P. Hlinka and J. Epstein (Army Chem. Centre, Md., U.S.A.) (*Anal. Chem.*, 1955, **27** [8], 1290-1293).—Dilute aq. soln. of ethyleneimine (I) or of *n*-butylamine (II) react with 1:2-naphthaquinone-4-sulphonate at pH 10.3 to give chloroform-extractable reddish dyes. Quant. estimations of the amines are made by absorbancy measurements at 450 $m\mu$ for II and 420 $m\mu$ for I on the $CHCl_3$ extracts. Ethanolamine also forms a reddish dye, which is extracted with isoamyl alcohol, and is measured at 420 $m\mu$. The Beer - Lambert law is obeyed over the range 0 to 4 p.p.m.

G. P. COOK

140. Use of γ [4]-(4-nitrobenzyl)pyridine as analytical reagent for ethyleneimines and alkylating agents. J. Epstein, R. W. Rosenthal and R. J. Ess (Army Chem. Centre, Md., U.S.A.) (*Anal. Chem.*, 1955, **27** [9], 1435-1439).—Colorimetric procedures are described for the determination of very low concn. of various ethyleneimines in water and various alkylating agents in a non-aq. solvent by the treatment of these compounds with 4-(4-nitrobenzyl)-pyridine, afterwards making alkaline. For ethyleneimine and substituted ethyleneimines the concn. range is from 0 to 5 p.p.m., and concn. of ethylamine and ethanolamine > 1000 times that of the imine concn. do not interfere. In non-aq. medium the method was applied to α -halogenated esters, diethyl sulphate, alkyl halides and various org. chlorides of As, P, S and N. Molar extinction coefficients are listed for 47 compounds.

G. P. COOK

141. Amperometric determination of ethylenediaminetetra-acetic acid with zinc ions. W. S. Wise and N. O. Schmidt (Imp. Coll. Trop. Agric., Trinidad, B.W.I.) (*Anal. Chem.*, 1955, **27** [9], 1469-1471).—A method for the determination of total and available EDTA (I) in soln. containing the Ca or Mg chelates is described. The soln. is titrated amperometrically at pH 4.6 with $ZnSO_4$ soln. for total I content. The available I content is titrated at pH 11.1, at which value Ca is not displaced from its chelate. If Mg is present, glycine is added to prevent the Zn displacing the

Mg from its chelate. Results, for added **I**, in the total and available **I** determinations were correct to $\pm 0.1 \times 10^{-5}$ mole of **I** at the 0.6 to 17×10^{-5} mole level. G. P. Cook

142. Sensitive determination of low-boiling organic sulphur compounds. J. A. R. Coope and G. J. Maingot (Univ. Brit. Columb., Vancouver, Canada) (*Anal. Chem.*, 1955, **27** [9], 1478-1479).—Methods are described for the determination of disulphide in organic soln. and for the direct determination of H_2S in the presence of thiols. The disulphide procedure is a modification of that of Bell and Agruss (*Ind. Eng. Chem., Anal.*, 1941, **13**, 297), marked improvements being obtained by using a stronger acid, reduced standard temp. and a time of heating sufficiently long to complete the reduction and direct all volatile thiol to the trap. The results are about 15 per cent. too high, but are reproducible to ± 1 per cent. and can be corrected by the use of a factor; the method is convenient for samples < 0.0003 mole. Determination of the H_2S is effected by separating pptd. CdS from mercaptides by adjustment of the acidity to pH 2.4 and then measurement of the CdS iodimetrically. The method is accurate to within a few per cent. in the range 0.002 to 0.01 per cent. of S. A method for the determination of thiols is also given. G. P. Cook

143. Paper chromatography of organophosphorus compounds. T. Weil (Israel Inst. Tech., Haifa, Israel) (*Helv. Chim. Acta*, 1955, **38** [5], 1274-1276).—Mixtures of phosphonous, phosphinic and phosphonic acids, and their isomers, were separated by an ascending paper-chromatographic method on Whatman No. 1 sheets (rolled into cylinders); 50 μ g of the substances (0.005 ml of a 1 per cent. alcoholic solution) were applied. The solvents used were collidine - H_2O , or butanol - 2 N aq. NH_3 . The spots were developed either by spraying with a 0.1 per cent. solution of phenol red in alcohol, adjusted to alkaline (purple) with 2 N NaOH, and subsequent stabilisation in NH_3 vapour (yellow spots on violet background); or by spraying with a saturated alcoholic solution of $AgNO_3$ and subsequent exposure to sunlight (white spots on a brown background). The R_F values of 15 organophosphorus compounds ($R \cdot P(OH)_2$, $R \cdot PO(OH)_2$ and $R_2 \cdot PO(OH)_2$), separated by both methods of elution, are tabulated. S.C.I. ABSTR.

144. Industrial analysis by optical methods. III. Analysis of trichlorobenzene by infra-red spectroscopy. Shinnosuke Saeki and Yoichiro Mashiko (*Rep. Gov. Chem. Res. Inst., Tokyo*, 1954, **49** [7], 241-245).—Three isomers of trichlorobenzene were spectroscopically analysed with the aid of key bands at 8.62 μ (for vicinal), 9.10 μ (for symmetrical) and 8.90 μ (for unsymmetrical). The sample was dissolved in CCl_4 to produce an ≈ 2 per cent. soln. and the absorption spectra were observed with an i.r. spectrograph (KBr type). The intensities of the bands were compared with those of the standard sample. The relationship between the resolving power of the spectrograph and the accuracy of measurements is discussed. The average deviation from the mean is ± 2 per cent. K. SAITO

145. Analytical determination of α -acetylbenzyl alcohol. L. Molnar and S. Bauer (*Chem. Zvesti*, 1953, **7** [5-6], 289-297; *Referativnyi Zh., Khim.*, 1955, Abstr. No. 5,848).— α -Acetylbenzyl alcohol (**I**), in products obtained by fermenting sugar soln. in the presence of benzaldehyde (**II**), is determined

by treating the sample with an excess of hydroxylamine hydrochloride and titrating the liberated HCl, by a potentiometric method, against NaOH soln. *Procedure*.—To 0.3 g of **I** add 25 ml of a 0.05 N ethanolic soln. of hydroxylamine hydrochloride, set aside for 30 min. and then transfer to a titration vessel, washing with 25 ml of ethanol. Add 5 ml of a saturated soln. of $CaCl_2$ and titrate potentiometrically against a 0.1 N methanolic soln. of NaOH, with a tellurium cathode and a platinum anode. An oscillographic method can be used to determine **I** and **II** in crude **I**. E. HAYES

146. Analysis of certain alkylated phenol mixtures by bromination. W. L. Spliethoff and H. Hart (State Univ., East Lansing, Mich., U.S.A.) (*Anal. Chem.*, 1955, **27** [9], 1492-1494).—By making use of the different number of *o*- or *p*-positions available for bromination in non-alkylated and alkylated phenols, the acid bromate-bromide method was successfully applied to the analysis of certain phenol mixtures, provided that a limited excess of Br and short bromination times were used. Recoveries of phenols from various mixtures were generally within ± 2.0 per cent. of the calculated result. G. P. Cook

147. Determination of nordihydroguaiaretic acid in creosote bush. J. O. Page (A. and M. Coll. Texas, College Station, Tex., U.S.A.) (*Anal. Chem.*, 1955, **27** [8], 1266-1268).—Machine-threshed fresh creosote bush is extracted with *n*-butyl ether, the solvent is drained off and then removed by steam-distillation, leaving a brown tacky residue which is extracted with boiling water. The boiling extracts are filtered and, on cooling the filtrate, crude nordihydroguaiaretic acid (**I**) separates out. This is filtered off and dried at 105°C. The filtrate is extracted with *n*-butyl ether to recover further small quantities of **I**; the procedure is as that described above. The crude **I** is purified by recrystallisation from a boiling aqueous soln. containing 0.25 per cent. of acetic acid and 0.1 per cent. of $NaHSO_3$, and remaining impurities are separated by adsorption on activated carbon from a similar boiling aq. soln. The pure **I**, m.p. 185° to 187°C, is completely pptd. from the cooled soln. and is filtered off, washed, dried and weighed. G. P. Cook

148. Spectrophotometric determination of esters in mixtures of benzyl benzoate and dibutyl phthalate. P. L. Davis and C. V. Bowen (U.S. Dept. Agr., Orlando, Fla., U.S.A.) (*Anal. Chem.*, 1955, **27** [8], 1233-1235).—Benzyl benzoate and dibutyl phthalate are determined in mixtures by measurement of the absorbancy at 230 $m\mu$ and the quantity of standard alkali required to saponify the esters. The concn. of the esters are calculated by application of a differential equation for which the absorptivity and the saponification constants of the components are required. Analysis of five known mixtures showed average recoveries of 100.08 per cent. for benzyl benzoate and 99.97 per cent. for dibutyl phthalate. Application to cloth patches impregnated with insect repellents containing these esters gave average recoveries of 101.4 per cent. for benzyl benzoate and 99.66 per cent. for dibutyl phthalate. G. P. Cook

149. Displacement of the nitro group during determination of nitrophenols and nitroanilines by the Koppeschaar method. L. D. Johnson, W. M. McNabb and E. C. Wagner (Univ. of Pa., Philadelphia, Pa., U.S.A.) (*Anal. Chem.*, 1955, **27** [9], 1494-1498).—On application of the Koppeschaar

method to the determination of 2:4-dinitrophenol and picric acid in mixtures it was found that picric acid consumes Br under the conditions of the procedure, resulting in a possible displacement of the nitro group with subsequent inaccurate titration. A modification is described in which both phenols are initially titrated and then the Koppeschaar procedure is applied to the titrated liquid to determine 2:4-dinitrophenol, the picric acid being calculated by difference. Results were accurate to within ± 0.3 per cent.

G. P. Cook

150. Improved procedure for preparation of 3:5-dinitrobenzoates of alcohols and phenols. R. E. Dunbar and F. J. Ferrin (N. Dakota Agric. College, Fargo, N. Dakota, U.S.A.) (*Chemist Analyst*, 1955, **44** [3], 77-78).—The sodium salt produced by the interaction of 1 ml of the hydroxy compound with sodium metal at room temperature, or if necessary by warming to 60° C, is treated with 0.5 g of 3:5-dinitrobenzoyl chloride; excessive heating should be prevented by cooling. The esters, which separate as solids on the addition of 10 ml of water, are washed with 10 ml of 2 per cent. Na_2CO_3 soln. and are recrystallised from acetone or alcohol.

O. M. WHITTON

151. Colorimetric determination of 2-hydroxy-4:6-dimethylpyrimidine. C. R. Szalkowski and W. J. Mader (Merck and Co., Rahway, N.J., U.S.A.) (*Anal. Chem.*, 1955, **27** [9], 1404-1408).—The method is based on the interaction of 2-hydroxy-4:6-dimethylpyrimidine (I) with sulphonic acid and sodium nitrite in ethanolic H_2SO_4 soln., which gives a red complex with absorption max. at 450 and 540 m μ . The latter wavelength is the more sensitive. With the exception of the 2-amino and 2-mercapto analogues the colour reaction is specific for I. Assay of pure and crude I and of Nicarbazin (a complex of I with 4:4'-dinitrocarbanilide) showed average deviations of $\approx \pm 0.25$ for the pure, ≈ 0.3 for the crude, and $\approx \pm 0.55$ per cent. for the crude hydrated material, and $\approx \pm 0.2$ per cent. for Nicarbazin.

G. P. Cook

152. Polarography of phenylmercury acetate. Takumi Kajimura and Shigeru Yamamoto (Yasugawa Lab., Sankyo Co.) (*Japan Analyst*, 1955, **4** [3], 152-156).—The polarographic reduction of phenylmercury acetate (I) was studied in buffer soln. of various pH values. The half-wave potential of the first reduction wave (-0.19 V vs. the S.C.E.) is practically independent of the pH value, but not that of the second wave (-1.14 V at pH 10). The wave height of both waves is proportional to the concn. of I within the range 1 to 10×10^{-4} M in 0.1 M KNO_3 containing gelatin and Sørensen's buffer soln. (pH 10). The sample (0.1 g) is dissolved in the buffer soln. (50 ml), a 1-ml portion of which is mixed with 9 ml of the regulating soln. (buffer soln.: M KNO_3 : 0.5 per cent. gelatin soln. = 75:5:2), and subjected to polarography at 25° C. The deviation from the mean is < 3.4 per cent. for samples of ≈ 90 per cent. purity.

K. SARO

153. Determining trace metals in petroleum distillates by an acid-extraction technique. J. E. Barney II (Standard Oil Co., Whiting, Ind., U.S.A.) (*Anal. Chem.*, 1955, **27** [8], 1283-1284).—The oil is extracted first with conc. H_2SO_4 by refluxing and then with a mixture of conc. HCl - acetone - water (2:1:1). The extracts are combined, evaporated to dryness, and then ignited until free from C. The inorganic matter is dissolved in conc. HCl, and the soln. is concentrated to about 0.2 ml and is trans-

ferred to graphite electrodes for spectrographic analysis with a direct-current arc. Recoveries of Cu, Fe, Pb, Mn, Ni and V from the oil were > 95 per cent., and the coefficient of variation of the method is 11 per cent. Application to an enriched gas oil was successful and the procedure is generally suited to fractions containing < 0.5 p.p.m. of metals.

G. P. Cook

154. Determining trace metals in petroleum distillates. Efficiency of recovery methods. J. E. Barney II and G. P. Haight, jun. (Standard Oil Co., Whiting, Ind., U.S.A.) (*Anal. Chem.*, 1955, **27** [8], 1285-1286).—Metals that may be present in petroleum distillates as organometallic complexes, especially porphyrins, are difficult to recover from the oil. Six methods were compared with the acid-extraction technique: (i) simple ashing, (ii) partial sulphated ashing, (iii) total sulphated ashing, (iv) extraction with iodine, (v) extraction with an HBr - acetic acid mixture, (vi) extraction with an HI - acetic acid mixture. Only (iii) and (v) and acid-extraction techniques gave quant. recovery of Cu, Fe, Pb, Ni and V.

G. P. Cook

155. Determination of trace metals in petroleum. Wet ash - spectrographic method. L. W. Gamble and W. H. Jones (Esso Stand. Oil Co., Baton Rouge, La., U.S.A.) (*Anal. Chem.*, 1955, **27** [9], 1456-1459).—A wet ashing - spectrographic procedure, in which $\text{Mg}(\text{NO}_3)_2$ is used, is described. Nickel, V and Mn can be accurately determined at the 0.1 to 2.0 p.p.m. level on 10 to 50-g samples, the standard deviations in p.p.m. being ± 0.05 , ± 0.02 and ± 0.06 for Ni, V and Mn, respectively. Close agreement is obtained with colorimetric methods. The determination of Fe, Na and Cu should also be possible if $\text{Mg}(\text{NO}_3)_2$ free of these elements were available.

G. P. Cook

156. Determination of trace Kjeldahl nitrogen in petroleum stocks. E. D. Noble (Calif. Res. Corp., Richmond, Calif., U.S.A.) (*Anal. Chem.*, 1955, **27** [9], 1413-1416).—A high sensitivity was obtained by (a) purification of the Kjeldahl reagents to give reproducible low blank values, (b) use of the phenol-sodium hypochlorite method for ammonia determination, modified to give improved reliability, and (c) studying the ability of the Kjeldahl procedure to convert trace amounts of N into NH_3 . The procedure permits the detection of 1 p.p.m. of total N in 5 g of sample and results are in good agreement with those of other methods.

G. P. Cook

157. Industrial analysis by optical methods. II. Analysis of petrol and its urea adduct by use of the molecular vibrational spectrum. Yoichi Mashiko (Rep. Gov. Chem. Res. Inst., Tokyo, 1954, **49** [7], 237-240).—A fraction (boiling range 90° to 110° C) of the distillate of crude oil was submitted to i.r. and Raman spectroscopy. The absorption bands (or Raman lines) were compared with those of pure hydrocarbons and their intensities were measured. *n*-Heptane, toluene, 2-methylhexane, methylcyclohexane and 1:3-dimethylcyclopentane were detected and their amounts estimated. The hydrocarbon separated by the urea adduct method was also examined in a similar way; it was found that it consists of *n*-heptane containing a small amount of toluene.

K. SAITO

158. Detection and quantitative determination of benzo[a]pyrene in American shale oil. H. J. Cahnmann (Nat. Cancer Inst., Nat. Inst. Health, Bethesda, Md., U.S.A.) (*Anal. Chem.*, 1955, **27** [8],

1235-1239).—The detection and quant. determination of benzo[a]pyrene in a typical sample of Colorado shale oil is described. The sample is vacuum-distilled and the fraction boiling between 400° and 510° C (corrected to 760 mm) is collected. The fraction is chromatographed on a Florisil column and is developed with cyclohexane until a blue fluorescent zone (observed in u.v. light) approaches the column exit. The receiver is changed when the refractive index of the cyclohexane eluate is the same as that of the pure solvent and the elution is continued with methanol. The receiver is changed again when a narrow dark-purple or purplish-brown zone is near the exit; the benzo[a]pyrene content of the fraction is determined by spectrophotometric measurement at 403 m μ . An alternative procedure for fractionation of the shale-oil distillate is also described and the benzo[a]pyrene content may also be determined by fluorescence spectrophotometry. The benzo[a]pyrene content of the sample was between 0.003 and 0.004 per cent. Recoveries between 97 and 100 per cent. were obtained from standard soln. of benzo[a]pyrene. G. P. COOK

159. Group-type nitrogen - hydrogen analysis of pyrrole-, indole-, and carbazole-type compounds. An infra-red absorption method. A. Pozefsky and I. Kukin (Gulf. Res. and Dev. Co., Pittsburgh, Pa., U.S.A.) (*Anal. Chem.*, 1955, **27** [9], 1466-1468).—An i.r. absorption method is presented for determining the approx. concn. of compounds of the HN= type of the pyrrole, indole or carbazole classes in materials such as Diesel oil. The absorptivities of six of these compounds in the 3480-cm⁻¹ region are reasonably constant and therefore permit a group-type method of analysis. Interference by hydrocarbons in the 3480-cm⁻¹ region is corrected by the application of a base-line technique, which gives results that are on the average \approx 11 per cent. low. G. P. COOK

160. The analysis of a few constituents of a high-boiling fraction of coal tar by means of infra-red absorption spectra. Hotoshi Kamada and Shigeyuki Tanaka (Tokyo Univ.) (*Japan Analyst*, 1955, **4** [4], 231-234).—The simultaneous determination of anthracene (max. absorption 11.41 μ), carbazole (8.05, 13.30 μ), phenanthrene (12.36 μ), fluorene (13.50 μ), acenaphthene (12.77 μ) and dibenzofuran (8.35 μ) in a high-boiling fraction of coal tar was studied in CS₂ soln. The extinction coeff. at the max. absorptions are compared with those of the standard sample. No significant interference results from the presence of other components of coal tar except in the determination of fluorene, which results in values too high owing to the absorption of benzene and acridine at 13.5 μ . The average deviation of the results from those obtained by the standard method is < 1.2 per cent. This method can be applied to the analysis of anthracene cake and of impurities in industrial anthracene and carbazole. K. SAITO

161. Quantitative estimation of phenol in coal tar. A. Marx and L. Rappen (*Brennst. Chem.*, 1955, **38** [15-16], 225-228).—A process is described which is suitable for the quantitative determination of phenol in coal tar, tar oils and other raw phenol mixtures, and which is more accurate, more rapid and simpler than the usual method of fractionating up to 191° C and determining the freezing point of the fraction. The method is unsuitable for works analysis. In principle the method consists in taking

a distillation fraction up to 204° C, mixing it with pure phenol of known freezing point (E_p), and taking the freezing point (E_g) of the mixture. The phenol content (in wt. per cent.) of the mixture is found from the expression $\left[\frac{E_g + 13}{0.54} \times (a + b) - b \times \frac{E_p + 13}{0.54} \right] \times \frac{1}{a}$ or by the simpler and sufficiently accurate form $[(1.852 \times E_g + 24.07) \times (a + b) - (1.852 \times E_p + 24.07) \times b] \times \frac{1}{a}$, where a is the wt. (g) of the fraction, and b is the wt. (g) and E_p the freezing point of the pure phenol added. As the sample fraction must be thoroughly dry it is heated with dry gypsum till no further increase in the freezing point occurs. The determination of E_g must be made accurately with a thermometer graduated to 0.02° C. A detailed description is given of the use of the method for determining the phenol content of (i) coal tars and tar oils (including a full description of a series of preliminary distillation and purification steps and of the preparation of the requisite fraction up to 204° C and (ii) various mixtures of phenol with cresols and xylois. Equations are given in each case for calculating the percentage of phenol in the starting materials from the observed E_g . H. L. WHITEHEAD

162. Analysis of nail lacquers. S. H. Newburger (Food and Drug Admin., Dept. Health, Washington, D.C., U.S.A.) (*J. Ass. Off. Agric. Chem.*, 1955, **38** [2], 524-532).—Nitrocellulose can be separated from dibutyl phthalate and arylsulphonamide-formaldehyde resin by benzene pptn.; the dibutyl phthalate is separated from the resin by extraction with light petroleum from 80 per cent. methanol. The three materials are then identified by means of their infra-red and ultra-violet spectra. The separation procedures, which are described in detail, afforded high results for nitrocellulose, low results for dibutyl phthalate, and recoveries of about 86 per cent. for the resin. Tritolyl phosphate, if present, is isolated with dibutyl phthalate; each can be identified and determined by means of the infra-red and ultra-violet spectra. A. A. ELDRIDGE

163. Identification of poly(vinylidene chloride) and its copolymers. J. H. Player (Brit. Cellophane Ltd., Bridgwater, England) (*Analyst*, 1955, **80**, 633).—The finely divided material (1 to 2 mg) is dissolved in 1 ml of freshly distilled pyridine, warmed if necessary. The cooled soln. is treated with 0.5 ml of saturated methanolic KOH. A dark brown-black colour and a ppt. indicate the presence of poly(vinylidene chloride). The colour produced by poly(vinyl chloride), as found by Wechsler (*J. Polymer Sci.*, 1953, **11**, 233), is a much lighter brown. A list of the copolymers of vinylidene chloride giving positive results with the test is given. The test can be applied to both unsupported films and coatings by placing a drop of pyridine on the surface of the material, followed by a drop of methanolic KOH. Poly(vinyl chloride) cannot be identified in the presence of poly(vinylidene chloride) by this test. A. O. JONES

164. Determination of benzoyl peroxide in poly(methyl methacrylate). I. Polarographic method. Tsugio Takeuchi, Naruto Yokouchi and Yuzi Takayama (Yamanashi Univ., Japan) (*Japan Analyst*, 1955, **4** [4], 234-237).—Benzoyl peroxide is polarographically reduced ($E_{\frac{1}{2}} = -0.26$ V vs. the N.S.E.) in a mixture of acetone and 0.25 M KNO₃ (9 + 1). The wave height is proportional to the concn.

within the range 2×10^{-5} to 4×10^{-4} M; a more concentrated soln. gives a max. at -0.4 V, which decreases the accuracy of the determination. Poly(methyl methacrylate) does not interfere with the polarogram. The sample (24 mg) is dissolved in 10 ml of the regulating soln. and submitted to polarography at room temp. Lithium chloride can be used as the supporting electrolyte but is no more satisfactory than KNO_3 . K. SAITO

165. **Saponification method for rosin esters.** A. E. Johnson and R. V. Lawrence (U.S. Dept. Agric., Olustee, Fla., U.S.A.) (*Anal. Chem.*, 1955, **27** [8], 1345-1346).—The saponification time of rosin esters is reduced by the use of hydrazine. *Procedure*—Weigh 1 g of the ester into a 250-ml saponification flask and add 25 ml of *n*-hexanol - KOH soln. (40 g of KOH and 20 ml of 85 per cent. hydrazine hydrate in 1 litre of *n*-hexanol). Reflux gently for at least 1 hr., cool, add 50 ml of neutral ethanol and titrate with HCl to phenolphthalein. Conduct a blank experiment in the same manner on the reagents. Saponification values were duplicated within ± 0.7 unit. Dark grades of rosin are bleached by the hydrazine so that the phenolphthalein end-point is easily seen with all samples. Eight rosin esters were successfully analysed.

G. P. COOK

166. **Analysis of lacquers containing nitrocellulose, alkyl resins and phthalate-type plasticisers.** M. H. Swann, M. L. Adams and G. G. Esposito (Aberdeen Proving Ground, Md., U.S.A.) (*Anal. Chem.*, 1955, **27** [9], 1426-1429).—Methods are described for the determination of nitrocellulose, total phthalate, phthalate ester plasticisers, non-volatile and phosphate ester content of lacquer compositions. Nitrocellulose is determined by pptn. from benzene soln. after prolonged refluxing to dissolve alkyl resins, and the total phthalic anhydride is determined on the filtrate as dipotassium phthalate. The content of phthalate ester plasticiser is determined by adsorption on charcoal, and the total phthalic anhydride content of lacquer vehicles is measured by a two-component u.v. spectrophotometric method. Phosphate-type plasticisers are determined by application of the molybdate pptn. method to the water-soluble products of a lacquer-KOH fusion. G. P. COOK

167. **Characterisation of inks by paper chromatography for criminological purposes.** C. G. Macris and M. D. Riganesis (Inst. Chem. and Microbiol., Athens) (*Anal. Chim. Acta*, 1955, **13** [2], 129-134).—Eight writing inks are examined by the circular-paper-chromatographic method of Rutter (*Brit. Abstr. C*, 1950, 1780). The quantities used correspond to the amount in one written character, and a mixture of *n*-butanol and acetic acid (1 + 1) is used as the developer. The effects of a number of reagents on the separated zones are noted, and these effects are also observed in u.v. light. The reagents used are aq. solutions of KOH, sodium dithionite in dil. aq. NaOH, H_2O_2 and $\text{K}_4\text{Fe}(\text{CN})_6$. W. C. JOHNSON

168. **Conductimetric determination of phenolic groups in mixtures such as isolated lignins.** K. Sarkanen and C. Schuerch (Coll. Forestry, State Univ. N.Y., Syracuse, N.Y., U.S.A.) (*Anal. Chem.*, 1955, **27** [8], 1245-1250).—A conductimetric method for the determination of phenolic groups in lignins and low-molecular-wt. phenols, the result of a study of the temp., time, concn. and solvent effects and phenolic structure, is described. The sample,

corresponding to a final concn. of 0.04 to 0.06 phenolic equivalent per litre, is added to the titration cell and 5 ml of acetone are added as solvent. Ethanol (96 per cent.) (10 ml) is added and finally 15 ml of water. The sample is then titrated with 2.5 N LiOH soln., the normal conductimetric technique being used, and the temp. being maintained at 20°C. Good results are generally obtained with monohydric phenols and phenol-carboxylic acids, and the values for several lignins compare well with those from other methods. Results from 25 different phenols and lignins are tabulated. G. P. COOK

169. **Detection of pentachlorophenol in treated wood.** S. S. Sakornbut and H. L. Morrill (Monsanto Chem. Co., St. Louis, Mo., U.S.A.) (*Anal. Chem.*, 1955, **27** [8], 1259-1261).—Sections of pentachlorophenol-treated wood are exposed to ClO_2 and are sprayed with a 1 per cent. soln. of crystal violet leuco base in xylene - Skellysolve E (1:1 by vol.). The pentachlorophenol is converted into chloranil (tetrachloro-*p*-benzoquinone), which oxidises the leuco base to crystal violet. During the development of the violet colour, oxidation by air is avoided by using an atmosphere of N or ClO_2 . The minimum pentachlorophenol concn. detectable in treated Ponderosa pine sapwood was 0.022 per cent. The method was used to determine the depth of penetration of the preservative into the wood.

G. P. COOK

170. **Identification of the colouring materials in shoe polishes and creams by paper chromatography.** J. Deshusses and P. Desbaumes (Lab. Cantonal de Chim., Geneva, Switzerland) (*Mitt. Lebensmitt. Hyg., Bern*, 1955, **46** [3], 258-260).—The dyes are first extracted from 0.2 to 0.3 g of the dried sample with boiling ethanol. The soln. is cooled, filtered and evaporated to dryness. The residue is extracted with water and then with light petroleum. The water-soluble dyes are chromatographed with the same solvents as those previously described for cosmetics (*Anal. Abstr.*, 1954, **1**, 1570; 1955, **2**, 1861, 3105). Formic acid (85 per cent.) - water (4:1 by vol.) is used as a solvent for the ether-soluble substances. W. H. PARR

See also Abstracts 20, 65, 66, 67, 276, 292.

4.—BIOCHEMISTRY

INCLUDING DRUGS, FOOD, SANITATION, AGRICULTURE

Blood, Bile, Urine, etc.

171. **Proposal for the distribution of a certified standard for use in haemoglobinometry.** R. K. Cannan (*J. Lab. Clin. Med.*, 1955, **46** [1], 135-140).—Under a proposal put forward by the U.S. Division of Medical Sciences, National Academy of Sciences (National Research Council) a limited number of standards are to be distributed without charge to clinical laboratories which undertake to meet certain minimum requirements for participation. The standards are three separate solutions containing certified concentrations of approx. 20, 40 and 60 mg of human haemoglobin in the form of cyanmethaemoglobin (I) per 100 ml. Details of the procedure for the determination of haemoglobin as I as well as details for calibrating another method in terms of the standard I are to be furnished with the standard. Independent comparison of

the standard with the British Standard is to be undertaken.

W. H. C. SHAW

172. Chromatographic estimation of four different human haemoglobins. T. H. J. Huisman and H. K. Prins (Univ. Groningen, Netherlands) (*J. Lab. Clin. Med.*, 1955, **46** [2], 255-262).—Two chromatographic procedures are given for the quantitative separation of human haemoglobins A, B, C and F on Amberlite IRC 50(XE64) resin. The first method requires conventional cylindrical columns and elution; the second, which is simpler and more rapid, utilises small flat-sided columns which are developed with a known vol. of eluent; the separated bands are then scanned optically and the concn. of each haemoglobin is determined from the optical density curve. Results compare favourably with those of existing methods.

W. H. C. SHAW

173. A simple, specific one-stage prothrombin assay using Russell's viper venom in kephalin suspension. P. Hjort, S. I. Rapaport and P. A. Owren (*J. Lab. Clin. Med.*, 1955, **46** [1], 89-97).—The simple, sensitive and specific test described is based on the time interval between recalcification of a test solution and clotting. A mixture of 0.2 ml each of adsorbed bovine plasma, Russell's viper venom - kephalin suspension and a dilution of the test plasma is incubated at 37° C for 5 min.; 0.2 ml of aq. CaCl_2 is then added and the clotting time observed. Details are given for the preparation of the reagents. Results are not affected by the presence of lipids, platelets, plasma thromboplastin, proconvertin, proaccelerin or fibrinogen.

W. H. C. SHAW

174. Estimation of heparin by titration with protamine. H. Kaller (Max-Planck-Ges., Göttingen) (*Arch. Int. Pharmacodyn.*, 1954, **99**, 163-174).—The estimation of the heparin content of a solution may be accomplished by adding protamine until the end-point is indicated by the clotting of a plasma sample. The amount of heparin in the solution is proportional to the amount of protamine used. The method is quick and accurate if certain controls are used.

CHEM. ABSTR.

175. An efficient clinical method for determining the carbon dioxide content of serum. A. Kahn (Dept. Med., Univ. Chicago, Ill., U.S.A.) (*J. Lab. Clin. Med.*, 1955, **46** [2], 312-317).—In the simple rapid method described, the pH of 1 ml of serum obtained anaerobically is measured; the serum is then equilibrated with a mixture of N containing a known amount (about 5 per cent.) of CO_2 and the pH is again measured. From the change in pH the CO_2 content of the sample is calculated or read from the nomogram given.

W. H. C. SHAW

176. An improved palladium chloride method for the determination of carbon monoxide in blood. T. H. Allen and W. S. Root (Columbia Univ., New York, U.S.A.) (*J. Biol. Chem.*, 1955, **216** [1], 319-323).—A spectrophotometric method is described for the determination of CO in 0.2 to 1.0 ml of blood. The results agree well with those obtained with a precise gasometric method. The CO is released from the blood by the addition of aq. $\text{K}_3\text{Fe}(\text{CN})_6$ soln. and saponin; it diffuses at atmospheric pressure into a second vessel where, at room temp., it reduces PdCl_2 to Pd. Addition of KI converts the unreduced PdCl_2 into soluble PdI_2 , and the extinction of the pink solution is determined at 490 m μ and is compared with that of standard solutions. A complete determination requires 3-5

hr.; the method needs no special apparatus and requires less skill than other methods.

J. N. ASHLEY

177. Polarographic determination of oxygen tension of whole blood. M. V. Tsao and C. H. Sloan, with J. Levinthal (Univ. Michigan, Ann Arbor, U.S.A.) (*J. Biol. Chem.*, 1955, **216** [1], 165-177).—A polarographic method, together with the apparatus, its construction, and the technique of working, are described for the direct determination of oxygen tension on 5 ml of saturated or non-saturated blood. The standard deviation of a single analysis for oxygen tensions of 30, 75 and 140 mm of Hg is 0.8, 1.4 and 2.0 mm of Hg, respectively.

J. N. ASHLEY

178. Colour production and stability in the Folin and Wu method of blood-glucose estimation. S. Dische (R.A.F. Inst. Path., Halton, Bucks., England) (*J. Clin. Path.*, 1955, **8** [3], 253-261).—To obviate the problem of fading of the final colour, a modified Folin and Wu method is recommended. To 4.6 ml of isotonic $\text{Na}_2\text{SO}_4 \cdot \text{CuSO}_4$ soln. (320 ml of 3 per cent. $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ + 30 ml of 7 per cent. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) add 0.1 ml of blood and 0.3 ml of 10 per cent. sodium tungstate, mix and centrifuge. To 2 ml of supernatant liquid add 2 ml of Folin and Wu's alkaline copper reagent, heat in boiling water for 6 min. and cool rapidly. Add 10 ml of molybdophosphoric acid reagent [130 ml of Folin and Wu's molybdophosphoric acid reagent + 25 ml of H_3PO_4 (sp.gr. 1.75) + 325 ml of water], mix and read with a red filter, together with a standard prepared similarly.

H. F. W. KIRKPATRICK

179. The effect of cations on reducing-sugar determinations with Shaffer and Hartmann's or Somogyi's reagents. T. A. Kilroe-Smith and J. F. De Gier (Transvaal and Orange Free State Chamber of Mines, Johannesburg, South Africa) (*Analyst*, 1955, **80**, 627-629).—The effects of different ions on the Shaffer and Hartmann micro-reagent and on the Somogyi reagent (compositions described) have been investigated. Three different salts, viz. CaCl_2 , MgCl_2 and FeCl_3 , were used and each had a profound effect on the reduction of glucose with each reagent. The results indicate that the effects noted are probably due to a change in the buffering power of the oxidising mixture, since the cations were able to form ppt. with the reagents. The concn. of these cations should therefore be maintained at a minimum in reducing-sugar determinations with these reagents. Ferric ions are particularly troublesome, probably owing to their oxidising power. Similar effects probably occur with any cations capable of altering the buffering capacity of the oxidising reagent.

A. O. JONES

180. 1:2-Diamino-4-nitrobenzene as a reagent for the detection and determination of alpha-keto acids in blood and urine. K. W. Taylor and M. J. H. Smith (King's Coll. Hosp. Med. Sch., London, England) (*Analyst*, 1955, **80**, 607-613).—A paper-chromatographic method for the separation of α -keto acids in blood and urine and the quantitative determination of pyruvic and α -oxoglutaric acids in blood is described. Blood is treated with HPO_4 , and centrifuged, the separated supernatant liquid is treated with a soln. of 1:2-diamino-4-nitrobenzene in HCl and, after 12 to 16 hr., the mixture is extracted with ethyl acetate. The nitro-quinoxalins formed are extracted from the ethyl acetate with Na_2CO_3 , the alkaline layer is acidified and re-extracted with ethyl acetate and the extract

is evaporated to dryness at 40° C. Urine is acidified, treated with the reagent and subsequently treated as for blood, the vol. of extractants being suitably reduced. The dry residue dissolved in acetone is subjected to descending paper-chromatography with a solvent mixture of ethanol, *n*-pentanol and aq. NH_3 . The areas of the paper occupied by the nitroquinoxalins are located under u.v. light, cut out and extracted with 30 per cent. aq. ethanol. Extinctions of the filtered extracts are determined at 280 $\text{m}\mu$. Calibration graphs are constructed from solutions in aq. ethanol of the pure nitroquinoxalins. Results of the determined blood levels of pyruvic and α -oxoglutaric acids are given and discussed.

A. O. JONES

181. The microbiological determination of vitamin B₁₂ in serum. R. Wolff, R. Karlin and P. Paysant (Lab. Chimie Physiol., Nancy, France) (*Bull. Soc. Chim. Biol.*, 1955, **37** [5-6], 735-738).—The method used by the authors (*Bull. Soc. Chim. Biol.*, 1953, **35**, 1409) gives values higher than those reported by other workers using very similar techniques. The difference is attributed to the presence of a thermolabile form of vitamin B₁₂ which is lost in the defecation procedure unless a small amount of HCN is previously added as in the authors' method.

H. F. W. KIRKPATRICK

182. Bound iron and unsaturated iron-binding capacity of serum; rapid and reliable quantitative determination. A. L. Schade, J. Oyama, R. W. Reinhart and J. R. Miller (*Proc. Soc. Exp. Biol. Med.*, 1954, **87** [2], 443-448).—**Reagents**—Prepare a phosphate buffer-ascorbic acid reagent (**I**) by adding 1 g. of ascorbic acid to 100 ml. of a mixture of $M \text{ H}_2\text{PO}_4$ and $M \text{ Na}_2\text{HPO}_4$ having a pH of 5.3. The final pH is 5.0. Dissolve 100 mg. of terpyridyl in 4 ml. of absolute ethanol and dilute to ≈ 40 ml. with water, clear by adding 0.20 *N* HCl, dropwise, and dilute to 100 ml. The final pH of this reagent is 4.3. Mix 4 parts of **I** with 6 parts of water to make reagent **A**, and 4 parts of **I** with 2 parts of terpyridyl reagent and 4 parts of water for reagent **B**. Prepare a stock standard soln. of Fe (1 mg. per ml.) by dissolving electrolytic Fe in a min. vol. of 10 *N* H_2SO_4 and diluting to vol. with water. Prepare a standard Fe-terpyridyl curve (0 to 2.4 μg of Fe per ml.) with dilutions of the stock standard soln. of Fe in 0.01 *N* HCl and under the conditions of the test. **Procedure**—Add 0.5 ml. of serum, by pipette, into each of two test-tubes. To one add 0.5 ml. of reagent **A** (control) and to the other 0.5 ml. of reagent **B** (test). Place both tubes in a water bath at 45° C for 20 min. and then read in micro-cuvettes of 1-cm path-length at 552 $\text{m}\mu$. The difference in the readings corrected for the reagent blank (0.5 ml. of reagent **B** + 0.5 ml. of water read against 0.5 ml. of reagent **A** + 0.5 ml. of water) referred to the standard curve gives the amount of bound iron in 0.5 ml. of the serum.

H. F. W. KIRKPATRICK

183. Electrometric urinometry. A. C. Corcoran (Georgetown Univ. Sch. Med., Washington, D.C., U.S.A.) (*J. Lab. Clin. Med.*, 1955, **46** [1], 141-143).—A comparison is made of sp. gr. and electrometric measurements for determining osmolality in urine concentration tests on patients with renal disease, in some of whom dietary Na was restricted. For routine examination of urines very low in Na the electrometric procedure is preferred.

W. H. C. SHAW

184. The determination of total base of urine with an ion-exchange resin conditioned as iodate.

J. C. Vanatta and R. M. Landers, jun. (Univ. Texas-Southwestern Med. School, Dallas, Texas, U.S.A.) (*J. Biol. Chem.*, 1955, **216** [1], 351-355).—Methods based on the use of iodate-conditioned resins are described for the determination of total base (total base before ashing) and total fixed base (total base after ashing) of urine. The method for the determination of total base in serum (Vanatta and Cushing, *Anal. Abstr.*, 1954, **1**, 2172) is satisfactory for urine but, when ashing is effected, the phosphates form insol. salts with Ca and Mg at the high temp. used; the serum method is therefore modified by pptn. of the phosphates with ferric alum before ashing. The total base is determined by the resin method. The error of the total fixed base in 16 replicate determinations is $< \pm 2$ per cent. Comparison of the values for total fixed base + NH_3 with those for the total base showed an average agreement of $+0.1$ per cent. (range, -1.6 to $+2.9$) on nine normal urines and on urines of six patients.

J. N. ASHLEY

185. A note on quantitative urobilinogen determinations. B. Balikov (Tercy-Jones Army Hosp., Battle Creek, Mich., U.S.A.) (*Clin. Chem.*, 1955, **1** [4], 264-268).—Watson's method for urobilinogen determination (*Amer. J. Clin. Path.*, 1944, **14**, 598) has been investigated for the effect on extraction of the acetic acid concn. in the final ferrous hydroxide filtrate. Optimum extraction was achieved by adjusting this concn. to 2 per cent. for urine and 1 per cent. for faecal extracts. Aliquots of the ferrous hydroxide filtrates are diluted to 49 ml (urine) or 49.5 ml (faeces) with water, 1.0 ml. or 0.5 ml. of glacial acetic acid is added and the method is completed as published. H. F. W. KIRKPATRICK

186. Modification of the Powell method for the separate determination of free and total bilirubin. H. E. Varizat (Rosario, Rep. Arg.) (*Act. Biochim.*, 1953, **2** [7], 16-19).—The Powell method as originally published (*Amer. J. Clin. Path.*, Techn. Suppl., 1944, **8**, 55) frequently gives rise to turbid solutions which falsify the colorimetric and photometric determinations. This drawback is overcome completely by using other buffers. For free bilirubin the soln. contains urea (24 g), KH_2PO_4 (0.9 g) and 0.067 *M* H_3PO_4 (18 ml) in 100 ml. For total bilirubin the soln. contains citric acid (15 g), trisodium citrate (5 g), caffeine (5 g), urea (24 g) and water to 100 ml.

CHEM. ABSTR.

187. Calcium determination in biological material. E. Y. Berger (Goldwater Mem. Hosp., Welfare Island, N.Y., U.S.A.) (*Clin. Chem.*, 1955, **1** [4], 249-252).—The Ca is pptd. as oxalate, excess of ammonium hexanitratocerate soln. is added and the excess of cerate is titrated with $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ soln., *o*-phenanthroline being used as indicator. Procedures are described for serum, heparinised plasma, urine, dried tissues and faeces.

H. F. W. KIRKPATRICK

188. An *o*-tolidine method for the detection of occult blood in faeces. J. Kohn and T. O'Kelly (Q. M. Hosp., Roehampton, England) (*J. Clin. Path.*, 1955, **8** [3], 249-251).—A stock soln. of *o*-tolidine, 4 per cent. in ethanol, is stable for a long period. For use, equal vol. of stock soln., glacial acetic acid and water are mixed. A portion of faeces about the size of a pea is boiled with 5 ml. of water and cooled; to 4 drops of reagent are added 1 drop of 20-vol. H_2O_2 and 1 drop of faecal suspension. A positive reaction is indicated by a green or blue colour appearing within 1 min. and

lasting from a few min. to several hr., according to the amount of blood present.

H. F. W. KIRKPATRICK

189. Quantitative determination of the different higher saturated fatty acids in fat from blood, chyle and faeces, by means of partition chromatography on rubber. J. H. van de Kamer, N. A. Pikaar, A. Bolssens-Frankena, C. Couvée-Ploeg and L. van Ginkel (Centr. Inst. Nutr. Res. T.N.O., Utrecht, Netherlands) (*Biochem. J.*, 1955, **61** [2], 180-186).—Methods are described for the extraction of fat and acids from blood, chyle and faeces, and for the hydrolysis of the fat, removal of unsaponifiable material, and purification and determination of the resulting fatty acids. The unsaturated fatty acids are first removed by oxidation with alkaline KMnO_4 , because they interfere with the separation of the saturated acids. The determination of hexanoic, octanoic, and decanoic acids, and of the unsaturated Δ^{13} -docosanoic acid before oxidation with KMnO_4 , and of the saturated acids, do-, tetra-, hexa- and octa-decanoic acids, eicosanoic, and docosanoic acids, after oxidation with KMnO_4 , is effected by reversed-phase partition chromatography by the method of Boldingh (*Brit. Abstr. C*, 1950, 325), with a column of powdered rubber.

J. N. ASHLEY

190. Determination of cyanide, thiocyanate and α -hydroxynitriles in plasma or serum. R. B. Bruce, J. W. Howard and R. F. Hanzal (Hazleton Labs., Falls Church, Va., U.S.A.) (*Anal. Chem.*, 1955, **27** [8], 1346-1347).—In a modification of the method by Aldridge (*Analyst*, 1944, **69**, 262) the cyanide and thiocyanate concn. are determined separately rather than the cyanide concn. being calculated by difference. The method is based on the conversion of cyanide and thiocyanate into cyanogen bromide by bromine water, the cyanogen bromide being subsequently treated with benzidine in pyridine to give an intense red colour, which is measured at 532 $\text{m}\mu$. α -Hydroxynitriles are hydrolysed to HCN by treatment with conc. NaOH soln. and are determined by the same colorimetric procedure. Recoveries of CN' from plasma averaged 99 per cent. (8 determinations) and of SCN' averaged 100 per cent. (4 determinations). The average recovery of lactonitrile in the presence of added CN' and SCN' was 89 per cent. (9 determinations).

G. P. COOK

191. The use of paper chromatography for *in vitro* studies of lactose metabolism in mammary gland preparations. R. Heyworth and J. S. D. Bacon (Dept. Biochem., Univ. Sheffield, England) (*Biochem. J.*, 1955, **61** [2], 224-232).—A method is described for the determination of lactose and for its separation from glucose and galactose by paper chromatography. The chromatograms are developed for at least 15 hr. with a mixture of butanol, acetic acid and water. The lactose is then eluted with hot water and is determined colorimetrically by the reducing-sugar method of Somogyi (*Brit. Abstr. C*, 1946, 42) and Nelson (*Brit. Abstr. C*, 1944, 191). The optical density of the colour obtained with the molybdo-arsenate reagent is measured with a Spekker absorptiometer with a Chance OR_2 (red) glass filter (50 per cent. transmission at 610 $\text{m}\mu$; 94 per cent. transmission at 650 $\text{m}\mu$). The amount of lactose is ascertained from a standard graph.

J. N. ASHLEY

192. The separation of sphingosine and related compounds by reversed-phase partition chromatography. J. B. Wittenberg (Western Reserve Univ.,

Cleveland, Ohio, U.S.A.) (*J. Biol. Chem.*, 1955, **216** [1], 379-390).—Sphingosine and related compounds are separated by reversed-phase partition chromatography on diatomaceous earth treated with dimethyldichlorosilane; the stationary phase is a mixture of chloroform and a hydrocarbon [isooctane or Skellysolve S (a decane fraction)] and the mobile phase is aqueous methanol. Before chromatography the compounds are converted into their N-succinyl derivatives. Compounds differing in the no. of hydroxyl groups, in methylation of one hydroxyl group, and in the degree of unsaturation have been separated. A new method is described for the determination of sphingosine and related compounds. They are converted into their N-succinyl derivatives by treatment with succinic anhydride, and the carboxyl group thus introduced is titrated with standard alkali. Amounts of 3 to 100 μmoles of sphingosine can be determined with an accuracy of 5 per cent.

J. N. ASHLEY

193. The action of purified alkaline phosphatases on di- and tri-phosphopyridine nucleotides. [Determination of these nucleotides in presence of each other.] R. K. Morton (Dept. Biochem., Univ. Cambridge, England) (*Biochem. J.*, 1955, **61** [2], 240-244).—A modification of the method of Racker (*Brit. Abstr. A*, 1950, 1670) is described for the determination of di- and tri-phosphopyridine nucleotides present together in one solution. The cuvette contains ethanolic hydrochloride (0.142 millimole) and aldehyde-free ethanol (2 millimoles) and, in addition, MgCl_2 (30 μmoles). Sufficient yeast alcohol-dehydrogenase to reduce completely 0.02 μmole of diphosphopyridine nucleotide in 3 min. is then added, and any change in optical density, due to this nucleotide, is determined. A solution (0.1 ml) of purified phosphatase ($\approx 10 \mu\text{g}$) from calf intestinal mucosa is then added, and the further change in optical density at 340 $\text{m}\mu$, due to the quant. conversion of tri- into di-phosphopyridine nucleotide, is measured. J. N. ASHLEY

194. Changes in lens during the formation of X-ray cataract in rabbits. [Determination of creatine phosphate.] A. Pirie, R. V. Heynning and P. H. Flanders (Nuffield Lab. Ophth., Univ. Oxford, England) (*Biochem. J.*, 1955, **61** [2], 341-347).—The procedure is based on the method of Slater (*Brit. Abstr. C*, 1953, 129) for the enzymic determination of energy-rich phosphate groups. Creatine phosphokinase prepared from rabbit muscle is added to the enzymic reaction mixture in the presence of an excess of hexose monophosphate. Creatine phosphate, in the presence of the kinase, reacts with adenosine diphosphate to form the triphosphate, and the enzymic analysis for energy-rich phosphate therefore includes creatine phosphate. In the absence of the kinase, or in the presence of *o*-iodosobenzoate (which inhibits the kinase), the creatine phosphate is not determined. The difference between the two determinations gives the amount of creatine phosphate. J. N. ASHLEY

195. Micro-determination of ester sulphate and free sulphate ions. P. W. Kent and M. W. Whitehouse (Biochem. Dept., Univ. Oxford, England) (*Analyst*, 1955, **80**, 630-631).—A method is described for the determination of esterified sulphate in sulphated muco-substances, applicable to 2- μg amounts of SO_4 . The samples of mucins or sulphated polysaccharides are heated with formic acid in sealed tubes at 105° C for 16 hr. Aliquots of the filtered hydrolysates or solutions of SO_4 in formic acid are

treated with a benzidine reagent and maintained at 0° C for 12 hr. The ppt., collected by immersion filters (construction described), is washed free from benzidine and dissolved in dil. HCl. The soln. is diazotised and coupled with thymol, and the colour is measured absorptiometrically, Ilford No. 603 filters (max. transmission at 485 m μ) being used. The calibration graph is prepared by diazotising and coupling known amounts of benzidine. Pptn. of benzidine sulphate is quant. in the range 2 to 30 μ g of SO₄²⁻. For 5 to 10 μ g the accuracy is within 10 per cent., and for 10 to 20 μ g within 5 per cent. When the method was tested with Na₂³⁵SO₄ and radioactive chondroitin sulphate all the measurable activity was found in the final diazotised soln.

A. O. JONES

196. The polarographic determination of dimethylnitrosamine in animal tissue. D. F. Heath and J. A. E. Jarvis (Med. Res. Council, Carshalton, Surrey, England) (*Analyst*, 1955, **80**, 613-616).—The tissue is homogenised with water, and proteins are removed by pptn. with sulphosalicylic acid and filtration. A portion of the filtrate is made 3 N with respect to NaOH and half is distilled, when all the dimethylnitrosamine is in the distillate. The distillate (2 ml) is placed in a thermostatically controlled polarographic cell with 0.2 ml of 0.1 M sulphosalicylic acid, deoxygenated by a stream of N and the polarogram is recorded. The graph of diffusion current against concn. is slightly curved. Recoveries from animals injected with dimethylnitrosamine are satisfactory. The min. amount that can be determined with an accuracy of \pm 0.05 μ g is 1 μ g. The use of the technique for other nitrosamines is discussed.

A. O. JONES

197. Determination of methylglyoxal in thiamine-deficient rats by paper chromatography. H. M. Salem (Fac. Agric. Cairo Univ., Egypt) (*Arch. Biochem. Biophys.*, 1955, **57** [1], 20-22).—The presence of methylglyoxal in the urine of thiamine-deficient rats is demonstrated by one-dimensional descending paper-chromatography with butanol-ethanol-water (40:10:50) as eluent and ammoniacal AgNO₃ as spray reagent.

W. H. C. SHAW

198. Detection of amino acids on paper chromatograms. J. A. Cifonelli and F. Smith (Univ. of Minn., St. Paul., Minn., U.S.A.) (*Anal. Chem.*, 1955, **27** [9], 1501-1502).—After oxidation by periodate, amino acids and other amino compounds can be detected on paper chromatograms by benzidine and starch-iodide reagents. The four procedures described enable certain of the amino acids to be classified. The *R_F* values for 18 amino compounds obtained by using mixtures of *tert*-amyl alcohol-*n*-propanol-water are listed.

G. P. COOK

199. Quantitative determination of amino acids by circular-paper chromatography. K. Krishnamurthy and M. Swaminathan (Central Food Tech. Res. Inst., Mysore, India) (*Anal. Chem.*, 1955, **27** [9], 1396-1399).—In the separation of 16 amino acids from a mixture, on a series of paper chromatograms, the following solvent mixtures were used: phenol-*n*-butanol-acetic acid, saturated with water, benzyl alcohol-*tert*-amyl alcohol, saturated with water, *n*-butanol-acetic acid, saturated with water, *m*-cresol saturated with a pH 8.4 buffer, and phenol saturated with a pH 12 buffer. The constituents of the unknown sample are identified by reference to a standard chromatogram. For quant. determinations, the chromatograms are treated with ninhydrin, the bands due to each acid are cut out,

the colour is extracted into 5 ml of 75 per cent. alcohol and is measured at 560 m μ . Highly reproducible results were obtained in the analysis of casein and were in close agreement with those reported by other workers.

G. P. COOK

200. The determination of amino acids in chromatograms with the aid of the ninhydrin reaction. T. S. Pashkina (Inst. Biol. and Med. Chem. Acad. Med. Sci. U.S.S.R., Moscow) (*Biokhimiya*, 1954, **19**, 702-712).—The ninhydrin reaction was applied in conjunction with the Troll and Cannan reagents (*J. Biol. Chem.*, 1953, **200**, 803). The procedures developed enabled the estimation of 95 per cent. of the amino acids in one-dimensional and 90 to 93 per cent. in two-dimensional chromatograms. It is claimed that by the new method sufficiently accurate amino-acid determinations can be made on spots from 0.05 micromole (0.7 μ g of N) and upwards. Proline and hydroxyproline are more easily determined by the isatin reaction. It is essential that the filter-paper is free from cationic metals and that the procedure is standardised with a high degree of precision.

CHEM. ABSTR.

201. Desalting amino-acid solutions by ion exchange. G. C. Mueller, G. Bowman and A. Heranen (Med. School, Univ. Wisconsin, Madison, Wis., U.S.A.) (*Anal. Chem.*, 1955, **27** [8], 1357-1358).—An ion-exchange method for desalting extracts of biological material, for amino-acid separation by paper chromatography, is described. The amino acids and cations (Na, K, Mg and Ca) are first adsorbed on a Dowex-50 (H form) column and the majority of amino acids are eluted free of inorganic salts with 0.8 N HCl in 55 per cent. ethanol. Fifteen amino acids are recovered quant. in this eluate; four additional amino acids are recovered from the column with aq. 6 N HCl after the selective elution of NaCl with aq. N HCl. Recovery of the amino acids ranged from 91 to 112 per cent.

G. P. COOK

202. Colorimetric detection and estimation of tryptophan. H. N. Antoniadis (Harvard Univ., Cambridge, Mass., U.S.A.) (*Chemist Analyst*, 1955, **44** [3], 78-84).—The procedure described is based on the characteristic red colour produced when a tryptophan soln. is layered on a soln. of Ce(SO₄)₂ in H₂SO₄. As little as 2 mg of tryptophan in 100 ml of sample can be detected by placing 1 or 2 ml of 0.1 N Ce(SO₄)₂-H₂SO₄ [34 g of Ce(SO₄)₂ in a mixture of 28 ml of conc. H₂SO₄ and 500 ml of water, to which a further 500 ml of water is added] in a test-tube, and introducing 1 ml of neutral sample soln. so that two layers are formed. For quant. determination, series of dilutions of the neutral sample soln. and of standard tryptophan soln. are prepared. It is assumed that the amount of tryptophan present in the dilution that will just form a red ring is equal to that in the last positive dilution of the standard soln. Although the test is not specific for tryptophan, none of the other org. compounds that gives the coloration is present in proteins or their hydrolysates.

O. M. WHITTON

203. A method of histidine determination based upon a modified Knoop reaction. II. A. Hunter (Research Inst., Hospital for Sick Children, Toronto, Canada) (*J. Biol. Chem.*, 1955, **216** [1], 391-394).—The method of Hunter (*Brit. Abstr. C*, 1953, 74) for the determination of histidine is modified to take into account the effects caused by the concn. of Br⁻ during bromination and the temp. at which

the colour is developed. The bromine reagent is prepared by dissolving Br (0.5 ml) in a mixture of *tert.*-butyl alcohol (50 ml) and 0.6 per cent. aq. KBr (50 ml). This solution is stable for one month if kept in the dark at 4° to 5° C. Bromination is carried out in a dark room under non-actinic illumination, and daylight is not admitted until after treatment with the arsenite reagent. All operations up to full development of the colour (completed 14 min. after addition of the acetate mixture) are carried out at $25^{\circ} \pm 0.2^{\circ}$ C. The final dilution of the coloured mixture to 10 ml is made with water at 10° C so as to delay, as far as possible, the gradual fading of the colour. The method gives good results with amounts of histidine as low as 0.04 mg and as high as 0.32 mg; the best results are obtained with 0.12 to 0.28 mg. The analytical samples should be diluted or concentrated until the histidine content (per 5 ml) is within these limits.

J. N. ASHLEY

204. The estimation of cysteine and cystine by potentiometric titration with mercuric chloride. R. Cecil (Univ. Oxford, England) (*Biochim. Biophys. Acta*, 1955, **18** [1], 154-155).—In the method described, mM cysteine hydrochloride is titrated with 0.1 M HgCl₂ at pH 1.2 to 6.7 in nitric acid, or acetate or phosphate buffers, with amalgamated gold electrodes. Cystine is treated with sodium sulphite at pH 6.5 to 7.0 for 30 min.; the soln. is then acidified with HNO₃ to pH < 2 and titrated similarly. Neither O nor Cl⁻ interfere.

W. H. C. SHAW

205. Precision obtained in the paper electrophoresis of serum proteins (statistical study). B. Drevon and R. Donikian (8 Ave. Rockefeller, Lyons, France) (*Bull. Soc. Chim. Biol.*, 1955, **37** [5-6], 605-612).—With a barbitone buffer of pH 8.6 and ionic strength 0.1, 29 determinations of the serum proteins by paper electrophoresis were carried out upon the same serum provided by a healthy male of 25 years of age. The apparatus was the Elphor H, and staining with Amido black 10B was carried out by the method of Kumagawa (*cf. Anal. Abstr.*, 1954, **1**, 3058). The paper was scanned photometrically and statistical interpretation of the results was made graphically. The coeff. of variation for the figures obtained for albumin and α_1 -, α_2 -, β - and γ -globulins were found to be 7.7, 26, 22, 16.2 and 13.9 per cent., respectively. To attain precision of this order at least three separate determinations must be made.

H. F. W. KIRKPATRICK

206. Cross-contaminator exclusion test for dry-ashing determination of protein-bound iodine. M. Samson, H. Brown and S. Eichen (Sampson Lab., Philadelphia, U.S.A.) (*Clin. Chem.*, 1955, **1** [4], 269-272).—Administration of iodinated compounds may increase the serum iodine to 500 μ g per cent. or more, so that the serum forms a potential source of cross-contamination in a series of tubes during the ashing stage. To eliminate such sera, mix 1 drop of each serum with 2 drops of 4 N Na₂CO₃ in test-tubes, dry and heat at 600° C in a muffle furnace for 2½ hr. To the ash add 1 drop of 4 N HCl and 1 drop of 0.15 N arsenous oxide soln. After 10 min. add 1 drop of 0.065 N ceric ammonium sulphate soln. and read the colours against a white background after 5 min. Decolourised tubes are potential cross-contaminators. The timing of this test is arranged so that > 30 min. is added to the time occupied by a series of 20 to 40 determinations.

H. F. W. KIRKPATRICK

207. Paper electrophoresis of lipoproteins. The staining of lipids with Sudan black. A. Nys (Univ. Hosp., Leuven, Netherlands) (*Chem. Weekbl.*, 1955, **51** [37], 643-644).—Sudan black selectively stains lipids but not proteins and is valuable for serum lipids and serum lipoproteins if experimental conditions are strictly observed. *Procedure*.—Prepare a saturated solution of Sudan black in 55 per cent. ethanol by bringing the solution just to the boil with constant stirring, cooling and filtering 2 or 3 times. Stain for 3 hr. at room temp. and wash by immersing each strip for 15 min. in 100 ml of 45 to 50 per cent. ethanol; use 60 to 100 cu. mm of serum for Whatman No. 1 paper 5 cm in width. Results with α_1 - and β -lipids are good and reproducible, but less favourable for α_2 -lipoproteins.

H. A. FISHER

208. Microchemical detection of characteristic functional groups in steroids. Side-chains. L. R. Axelrod (Univ. School Med., Rochester, N.Y., U.S.A.) (*Anal. Chem.*, 1955, **27** [8], 1308-1311). Methods of applying in succession known chemical reactions to micro quantities (< 60 μ g) of steroids on filter-paper and then identifying from the derivatives the known side-chains of adrenocortical and sex hormones are described. Periodic acid, lead tetra-acetate, acetic anhydride, CrO₃, lithium aluminium hydride, aluminium isopropoxide, triphenyltetrazolium chloride and *m*-dinitrobenzene were applied for the identification of nine side-chains. Schemes for identification are illustrated.

G. P. COOK

209. Fluorimetric determination of Δ^4 -3-ketosteroids. D. Abelson and P. K. Bondy (Yale Univ. Sch. Med., New Haven, Conn., U.S.A.) (*Arch. Biochem. Biophys.*, 1955, **57** [1], 208-217).—The simple method described is based on the formation of fluorescent compounds when Δ^4 -3-ketosteroids are treated with 0.1 to 0.3 N potassium *tert.*-butoxide in *tert.*-butanol. Quantities from 0.1 to 10.0 μ g of steroid may be determined and 0.01 μ g detected with 0.5 ml of the reagent. The method is applicable to testosterone, progesterone, cortisone and other biologically active C₂₁-corticosteroids.

W. H. C. SHAW

210. Infra-red spectra of adrenocortical hormones, in potassium bromide discs. A. L. Hayden (Nat. Inst. Health, Bethesda, Md., U.S.A.) (*Anal. Chem.*, 1955, **27** [9], 1486-1489).—The i.r. spectra of six adrenocortical hormones dispersed in KBr discs are presented. The spectra are reproducible and can be used for identification purposes. Corticosteroids possessing a 17-hydroxyl group, and those in which this group is absent, exhibit significant differences in the 1100 to 1000-cm⁻¹ region.

G. P. COOK

211. Separation of corticosteroids by counter-current distribution. H. Carstensen (Univ. Inst. Physiol., Uppsala, Sweden) (*Acta Chem. Scand.*, 1955, **9** [6], 1026-1027).—Six corticosteroids have been shown to be separable by 24 to 48 countercurrent transfers. Partition coefficients (*K*) for different systems of solvent pairs were calculated from the countercurrent distribution data by Way and Bennett's method (*J. Biol. Chem.*, 1951, **192**, 335). Fairly good separation is obtained if the separation factor β (*i.e.*, the ratio of higher to lower *K* of a pair of solutes) exceeds 3 in 24 transfers or 2.6 in 48 transfers. Nine different solvent systems are given, but no single one of these is sufficient to separate all the six corticosteroids investigated. The most favourable β value of 2.35 was obtained in a system comprising the phases 20 per cent.

ethanol + 80 per cent. H_2O with 0.05 per cent. (w/v) NaCl, and 70 per cent. CCl_4 + 30 per cent. n-hexane (at 22-0° C). Numerical data obtained in various solvents are tabulated. P. HAAS

212. Estimation of hydrocortisone secretion. Method of calculation from urinary-excretion data.

R. H. Silber (Merck Inst. Ther. Res., Rahway, N.J., U.S.A.) (*Clin. Chem.*, 1955, **1** [4], 234-240).—Activity of the adrenal cortex is in general reflected in the excretion of 17:21-dihydroxy-20-ketosteroids (I). There is a possibility that in certain conditions adrenal output of hydrocortisone may be altered without significant change of steroid concn. in blood and urine. A method has therefore been devised to estimate the adrenal output of hydrocortisone from urinary-excretion data. Normal subjects were given graded doses of 0 to 50 mg of hydrocortisone (free alcohol) orally on consecutive days; urine was collected for 8 hr. after each dose and I was determined by the method of Silber and Porter (*Anal. Abstr.*, 1955, **2**, 142). The basal excretion was found by extrapolation of the results and the fraction of the test dose excreted was calculated; the adrenal secretion (8 hr.) = basal excretion/fraction excreted. Five subjects secreted an average of 13.8 mg of hydrocortisone in the 8-hr. period. ACTH increased the secretion, whereas aspirin, ascorbic acid and thenylldiamine (tripelennamine) appeared to be without effect.

H. F. W. KIRKPATRICK

213. The interconversion of serine and glycine: participation of pyridoxal phosphate. [Determination of enzyme activity.] R. L. Blakley (*Biochem. J.*, 1955, **61** [2], 315-323).—A method is described for the determination of the activity of the enzyme (from rat liver) that synthesises serine from glycine and formaldehyde in the presence of tetrahydropteroylglutamic acid. The synthesis is carried out under specified conditions in Warburg vessels, and the amount of serine produced in a given time is determined manometrically by measurement of the CO_2 liberated after oxidation with $NaIO_4$.

J. N. ASHLEY

214. The colorimetric determination of leucine aminopeptidase activity with L-leucyl-2-naphthylamine hydrochloride. M. N. Green, Kwan-Chung Tsou, R. Bressler and A. M. Seligman (Harvard Med. Sch., Boston, Mass., U.S.A.) (*Arch. Biochem. Biophys.*, 1955, **57** [2], 458-474).—An aliquot of a tissue homogenate or serum sample is incubated for 2 hr. at 37° C with aq. L-leucyl-2-naphthylamine hydrochloride (I) at pH 8.2. The 2-naphthylamine, liberated in proportion to the amount of leucine aminopeptidase in the sample, is then determined colorimetrically by coupling directly with tetrazotised o-dianisidine or by diazotisation and subsequent coupling with N-(1-naphthyl)ethylenediamine hydrochloride. Trypsin, chymotrypsin and pepsin do not interfere. Details are given for the preparation of I and of related compounds. W. H. C. SHAW

See also Abstracts 15, 17, 84, 219.

Drugs

215. Quantitative paper-chromatographic determinations of alkaloids by measurement of spot area. O.-E. Schultz and D. Strauss (Univ. Tübingen, Ger.) (*Dtsch. ApothZtg.*, 1955, **95** [27], 642-644).—Paper-chromatographic determinations of alkaloids

(by an ascending method) have been demonstrated on morphine and strychnine (5 to 100 μg) and a method of planimetric evaluation of the developed spots is described. Mixtures of butanol - glacial acetic acid - water (100:20:53.5, by vol.) and butanol - 96 per cent. formic acid - water (120:20:70) are used as solvents; morphine is developed with a ferric chloride - ferricyanide reagent, and strychnine with a modified Dragendorff reagent (preparation given). The extracted alkaloid in 0.1 N HCl is placed on the starting line. Factors that cause variations of spot areas have been examined and their effects ascertained, i.e., vertical range (71 to 245.5 mm), time of ascent (2 to 48 hr.), period of saturation of paper before development (0 to 60 hr.), area of initial spots on starting line, spray reagent and solvent. The relation between spot area (in sq. mm) and amount of substance (log of alkaloid contents in μg) is illustrated by graphs and the best conditions for planimetric evaluation are tabulated. The method was found suitable for low concentrations of alkaloids (40 to 80 μg) and small vertical ranges (100 to 130 mm) in determinations where an accuracy of ± 10 per cent. is sufficient. S.C.I. ABSTR.

216. Turbidimetric determination of nicotine. An analytical application of Valser's reagent.

R. H. Robinson (Fisher Scientific Co., Pittsburgh, Pa., U.S.A.) (*Anal. Chem.*, 1955, **27** [8], 1351-1353).—A method for the determination of nicotine in the presence of nornicotine is described. The nicotine is pptd. as nicotine mercuric iodide in 0.2 N H_2SO_4 with potassium mercuric iodide (Valser's reagent) and measured turbidimetrically by comparison with standards in a photometer; the turbidity is stabilised by the addition of starch soln. Nornicotine in amounts > 37 times the nicotine concn. do not interfere at the level of 4 μg per ml. A detailed method for the determination of nicotine in tobacco and insecticides with this procedure is described, and close agreement with the A.O.A.C. procedure is obtained. G. P. COOK

217. A method for the estimation of reserpine in samples of Rauwolfia alkaloids.

M. M. Dhar and S. Bhattacharji (*J. Sci. Ind. Res., B, India*, 1955, **14** [6], 276-278).—The method is based on the spectrophotometric determination of 3:4:5-trimethoxybenzoic acid (I) liberated from reserpine by alkaline hydrolysis. Procedure—An aliquot of the liberated I is chromatographed on paper in a 2 per cent. aq. NH_3 - n-butanol system and eluted with 0.1 N aq. NH_3 . From the extinction values of the eluates at 254 $m\mu$ (I shows maxima at 253 to 254 $m\mu$, $\log \epsilon = 3.9062$), the quantity of reserpine, corresponding to the liberated I, can be calculated directly. G. C. JONES

218. Chromatographic separation of adrenaline and noradrenaline.

V. Carassiti and A. M. Ferrero (*Boll. Sci. Fac. Chim. Ind. Bologna*, 1955, **13** [2], 37).—Adrenaline and noradrenaline may be separated by paper chromatography. A circular horizontal technique has been used, with a methanol-1 per cent. aq. tartaric acid (19:1) solvent. The respective R_F values are 0.75 and 0.68. The substances are made visible by treatment on the paper without drying, with a few drops of conc. aq. NH_3 , and observation under Wood's light. The former gives a yellow fluorescence and the latter blue-violet. A few μg of each base may be detected. L. A. O'NEILL

219. Assay of intrinsic factor preparations: comparison of the hepatic uptake of radioactive ^{60}Co -B $_{12}$ with the hematopoietic response in pernicious anaemia. G. B. J. Glass, L. J. Boyd, A. L. Lohby and L. Stephanson (*J. Lab. Clin. Med.*, 1955, **46** [1], 60-73).—The method described is based on the determination of radioactivity of the liver after the oral administration of an intrinsic factor preparation to a patient with pernicious anaemia, together with a standard dose of 0.5 to 2 μg of ^{60}Co -labelled vitamin B $_{12}$. The radioactivity, recorded externally over the liver region of such patients by means of a scintillation counter six and seven days after administration, is a measure of the amount of the intrinsic factor in the dose of the preparation under test. Good correlation is obtained between results by the method described and those obtained by measurement of reticulocyte and red-cell responses in patients with pernicious anaemia in relapse. W. H. C. SHAW

220. Examination of commercial rhubarb extracts. VIII. Anthraquinones. H. Auerhoff (*Disch. ApothZtg*, 1955, **95** [27], 644-645).—It is suggested that, since extracts of rhubarb containing rhaponticin have but slight pharmacological effect, they should be rejected. Two simplified paper-chromatographic methods for detecting the presence of rhaponticin in commercial rhubarb preparations are described, together with the determination of anthraquinones in rhaponticin-free rhubarb extracts. A weighed amount of the extract ($\approx 50\text{ mg}$) is boiled with 7.5 ml of glacial acetic acid for 15 min., then dissolved in ether by refluxing with 30 ml for 15 min., decanting through a cotton plug and treating the residue with another 30-ml portion of boiling ether for 10 min. The ether solutions (in a 300-ml separating funnel) are extracted with 15 ml of 30 per cent. NaOH and 60 ml of 5 per cent. NaOH containing 2 per cent. of aq. NH_3 and washed with 10 ml of the NaOH-aq. NH_3 mixture. The combined red alkaline extracts are made up to 100 ml and heated on a steam bath for 2 hr. After the soln. is cooled the colour is compared with that of a suitably prepared standard solution of 1:8-dihydroxyanthraquinone, in a Pulfrich photometer (filter S53, 5-mm cuvettes) and the total anthraquinone is calculated with the aid of a control curve, calibrated with 2 mg of anthraquinone in 100 ml ($E = 0.43$) and 4 mg per 100 ml ($E = 0.84$), or in a Lange colorimeter (glass filter VG9, 100-ml cuvettes, dilution 10 + 90), and the anthraquinone calculated by means of control curves, calibrated with 0.1 mg of anthraquinone per 100 ml ($E = 0.085$) and 0.3 mg per 100 ml ($E = 0.24$).

S.C.I. ABSTR.

221. New chemical method for the determination of penicillin. G. Tokár, I. Simonyi, G. Gál (*Magyar Kém. Foly.*, 1955, **61** [5], 146-149).—Fehling's reagent reduces the amide nitrogen in penicillin or its derivatives with the evolution of NH_3 , which is then determined. *Procedure*—Weigh into the Schulek-Vastagh ammonia-distillation apparatus (*Z. anal. Chem.*, 1931, **84**, 167) 0.4 g of potassium penicillin-G (I), or 0.3 g of procaine penicillin-G (II) or 0.45 g of benzathine penicillin-G (III). Add 40 ml of Fehling's solution. With slow boiling distil 80 per cent. of the soln. into 0.1 N HCl (20 ml) and determine the ammonia in the usual way. One ml of 0.1 N HCl \equiv 0.0372 g of I or 0.0294 g of II or 0.0454 g of III. An identical process can be used for lower concn; the Fehling's

soln. is made from equal vol. of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (6 g) in 1 litre of H_2O and NaOH (4.5 g) and 10 g of K H tartrate (10 g) in 1 litre of H_2O . Oil-containing preparations are saponified by adding 30 per cent. aq. NaOH (5 ml) to the sample; $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ (0.3 g) is added to control foaming.

A. G. PETO

222. Fractionation of crude fumagillin by distribution methods. R. R. Goodall and J. K. Landquist [I. C. (Pharm.), Manchester] (*Analyst*, 1955, **80**, 499-502).—A crude extract with amoebicidal properties separated from *Aspergillus fumigatus* (strain A61) was separated by a chromatographic method into the known antibiotic fumagillin and a product "thiogillin" containing as its major constituent a substance related to gliotoxin. A counter-current fractionation of thiogillin, with light petroleum-benzene and ethanol-water as solvent systems, with subsequent absorptometric examination showed the presence of three fractions, of which one only had amoebicidal properties; this was identified as fumagillin. An improved method for bulk purification of fumagillin was developed depending upon its acidic properties. Separation from neutral or less acidic impurities was achieved by distribution between a solvent and an aq. borax buffer (pH 9), the fumagillin being finally extracted from the aq. phase and crystallised from acetone.

A. O. JONES

223. Detection and quantitative estimation of thiobarbituric acid derivatives. E. Heise and K. H. Kimbel (*Arzneimittel-Forschung*, 1955, **5** [3], 149-151).—New colour reactions, modifications of Zwikker's reactions (*Pharm. Weekbl.*, 1930, **68**, 975; 1931, **69**, 1178), are described. To a methanolic solution of the barbiturate is added either a saturated methanolic soln. of CoCl_2 followed by a pellet of KOH, or a 10 per cent. aqueous soln. of CuSO_4 followed by pyridine, the coloured solution so formed being extracted with chloroform. Barbiturates, thiobarbiturates and thiourea derivatives can be distinguished and a quant. colorimetric method based on the former reaction has been developed; 0.002 to 0.01 M solutions of the barbiturate are used.

P. S. STROSS

224. Detection of antipyrine [phenazone] and 1-naphthylamine. F. Feigl, C. C. Neto and E. Silva (Min. Agric., Rio de Janeiro, Brazil) (*Anal. Chem.*, 1955, **27** [8], 1319-1320).—Nitrosophenazone condenses in acetic acid soln. with 1-naphthylamine to give a violet azo dye, and this reaction is used as the basis of a specific test for both compounds. *Procedure for phenazone*—Mix 1 drop of the sample, 1 drop of glacial acetic acid and 1 drop of 5 per cent. NaNO_2 in a small test-tube. After occasional shaking during 5 min. add a pinch of sodium azide and set aside until there is no further evolution of gas. Add several mg of solid 1-naphthylamine hydrochloride and heat in boiling water for a few min. A violet colour, of intensity depending on the phenazone concn., develops, the limit of detection being 2 μg . *Procedure for 1-naphthylamine*—Add 1 drop of the reagent soln. to 1 drop of the sample in acetic acid soln. and warm at 100°C. The reagent is prepared by dissolving 1 g of phenazone in 20 ml of acetic acid (1:1) and 0.6 g of NaNO_2 is added. After 10 min., 0.5 g of sodium azide is added and the volume is diluted to 150 ml with acetic acid (1:1). The limit of detection is 0.5 μg .

G. P. COOK

225. Ion-exchange chromatographic and spectrophotometric determination of antihistamines. S. M. Blaug (*Dissert. Abstr.*, 1955, **15** [6], 983-984).—Antihistamine compounds are liberated for titration by passing the alcoholic solution of their salts through a basic exchange resin. If inorganic salts are present (e.g., in pharmaceutical preparations) the resin must be only weakly basic. Ephedrine, if present, must be removed by prior treatment on a cation-exchange resin. Ultra-violet absorption spectra have been plotted for 10 antihistamines and used in determining them alone or in pairs.

A. R. PEARSON

226. Colorimetric determination of Conteben [thiacetazone]. F. Icha, R. Kalvoda and J. Zýka (*Českosl. Farmac.*, 1954, **3** [7], 244-246. *Referativnyi Zh., Khim.*, 1955, Abstr. No. 7,696).—Thiacetazone is hydrolysed with HCl and the *p*-acetamidobenzaldehyde formed is condensed with 2:4-dinitrophenylhydrazine in methanol. The hydrazone soln. is made alkaline with an excess of methanolic NaOH soln., and the intensity of the wine-red colour which develops is measured in a colorimeter fitted with a green filter. For concn. of thiacetazone of 1×10^{-5} to 1.2×10^{-4} , Beer's law is obeyed.

E. HAYES

227. Assay of ephedrine in tablets of aminophylline with phenobarbitone sodium. S. Bhattacharya and K. Roy (*J. Inst. Chem., India*, 1955, **27** [2], 128-130).—An aliquot part (≈ 50 mg of ephedrine hydrochloride) of a filtered soln. containing 20 tablets dissolved in 15 ml of 10 per cent. aq. NH_3 and 185 ml of water is placed in a separating funnel, saturated with NaCl, and 5 ml of *N* NaOH are added. Liberated ephedrine is extracted with ether, filtered, and treated with 10 ml of 0.1 *N* H_2SO_4 . Excess of acid is titrated with 0.02 *N* NaOH to methyl red.

E. G. BRICKELL

228. Determination of aluminium and calcium contents in Liquor Aluminiumi Acetici D.A.B. VI. B. Schmitz (*Dtsch. ApothZtg.*, 1955, **95** [27], 637-640).—The official gravimetric determination of Al in Liquor Aluminiumi Acetici (D.A.B. VI) is criticised and other methods, including the quant. pptn. of Al oxinate, are reviewed. A new process of determining basic Al and Ca acetates in the presence of each other is presented and recommended for accuracy and speed. The content of Ca of the test solution (25 g of Liquor Aluminiumi Acetici made up to 200 ml with H_2O and buffered with borax to pH 8) is determined by titration with EDTA (disodium salt) (I), murexide being used as indicator. In another identical dilution of the test substance the sum of Al and Ca is determined by adding 20 ml of 0.1 *M* I, heating the turbid mixture to 80° C until clear, cooling to between 1° and 3° C, adding buffer solution and back-titrating the excess of I against Eriochrome black T as indicator until the steel-blue colour of the solution changes to wine-red. Subsequent reversion of colour is disregarded.

S.C.I. ABSTR.

229. Application of flame spectrophotometry to the analysis of medicaments. I. Apparatus and methods. J. Dorche, M. Rollet and C. Costet (*Ann. Pharm. Franç.*, 1955, **13** [4], 283-287).—The requirements of a flame photometer are discussed; the authors use the oxy-acetylene flame photometer of Jobin and Yvon. The wavelengths used and limits of detection obtained are: Ba 873 m μ , 14 p.p.m.; B 520, 10; Cu 423, 0.48; Cr 427, 2; Cu 325, 12; Fe 373, 17; Li 671, 0.035; Mg 383, 48;

Mn 403, 1.7; Pb 405, 186; K 768, 0.23; Ag 338, 77; Na 589, 0.035; Sr 461, 0.34. **II. Medicaments containing salts of alkali metals.** J. Dorche, M. Rollet and C. Costet (*Ibid.*, 1955, **13** [4], 288-297).—The interference of anions (found to be negligible), of acids, and of organic compounds (some, e.g., alcohol, give reproducible disturbances, but others, e.g., sugars, give imprecise interferences) are investigated. A 10:1 excess of Na over K gives a 15 per cent. greater reading for the K line at 768 m μ , which is greater than the emission of the same amount of Na at that wavelength. The mutual influence of Na, K and Li is investigated; Ca and Ba interfere slightly with Li at 671 m μ and Na at 589 m μ , but the amount is only that due to their own emissions in these regions. With K the reading is increased both by the alkaline-earth emissions and enhanced emission of the K. To detect Na, K and Li in a mixture it is advisable to take readings slightly above and below as well as at the appropriate wavelength of the line. For quant. work it is always necessary to prepare standards with nearly the same content of interfering substances as the test material.

E. J. H. BIRCH

See also Abstracts 151, 152, 261.

Food

230. The determination of crude fibre. III. V. P. Hirsjärvi (Agrikulturchem. Lab., Helsinki, Finland) (*Z. anal. Chem.*, 1955, **147** [2], 81-86).—The method of Hirsjärvi and Andersen (*Anal. Abstr.*, 1954, **1**, 1648) for the determination of crude fibre is not suitable for hay and feed yeast. Both this method and that of Puranen and Tomula (*Acta Chem. Fenn.*, 1930, **3**, 85) give lower results than the Weender method, and the Weender method is recommended for these materials; the use of a glass-wool filter is advantageous with yeast. The discrepancies between the different methods are not related to the fineness of the samples tested. **IV.** V. P. Hirsjärvi (*Ibid.*, 1955, **147** [2], 86-99).—Several methods for the determination of crude fibre in feeding-stuffs containing large amounts of calcium compounds are examined for accuracy and reproducibility; results obtained by the Weender method before incorporation of the calcium compounds are used as a basis for comparison. The methods of Mach and Lepper (*Landwirtsch. Versuchsstat.*, 1926, **104**, 313) and Hirsjärvi and Andersen (*Anal. Abstr.*, 1954, **1**, 1648) give satisfactory results; the second method is more rapid and more practicable. It is recommended that a glass-wool filter be used in both methods (see *Anal. Abstr.*, 1954, **1**, 1648).

E. HAYES

231. The filtration of crude fibre. H. Thaler (Dtsch. Forschung. Lebensmittelchem., Munich, Germany) (*Mitt. Lebensmitt. Hyg., Bern*, 1955, **46** [3], 251-254).—The use of a sintered-glass crucible covered with a pad of paper pulp for filtration was found to give improved results in the Fincke and Thaler method for estimating crude fibre.

W. H. PARR

232. Determination of sucrose and lactose in chocolate. P. Raymond (Lab. de N.V.P. de Gruyter en Zoon, Bois le Duc, Netherlands) (*Mitt. Lebensmitt. Hyg., Bern*, 1955, **46** [3], 246-250).—To a weighed amount of the chocolate (16.269 g or 26.026 g for Laurent or Ventzke scales, respectively) are added 100 ml of H_2O and 0.5 g of Na_2CO_3 and the mixture is kept at 50° to 60° C for 20 min. It is then

clarified with a neutral soln. of Carrez reagent [25 ml of 3.6 per cent. $K_4Fe(CN)_6 \cdot 3H_2O$, 25 ml of 7.2 per cent. $ZnSO_4 \cdot 7H_2O$ and 50 ml of 0.1 N NaOH]. The soln. is filtered and the first 25 ml are discarded. Sucrose is estimated from the optical rotation before and after inversion. The lactose is determined by the compleximetric method of Potterat and Eschmann (*Anal. Abstr.*, 1955, 2, 1327) with slight modifications. W. H. PARR

233. An examination of Scottish heather honey.

II. T. J. Mitchell, L. Irvine and R. H. Scoular (Royal Tech. Coll., Glasgow, Scotland) (*Analyst*, 1955, 80, 620-622).—Previous examination of 42 samples of honey, of which 30 were predominantly ling honey, showed evidence of a relationship between the colloid content, total N and thixotropy (Mitchell *et al.*, *Anal. Abstr.*, 1954, 1, 2803). Since the high colloid content of ling honey has been shown to be the cause of thixotropy (Pryce-Jones, *Proc. Linn. Soc. Lond.*, 1944, 2, 129) the nature of the colloid is of interest. In 25 samples of ling honey and one of bell-heather honey, the nitrogen content, pH, moisture and thixotropy were determined. The pH ranged from 4.20 to 5.36 for the ling honeys, and was 4.14 for the bell-heather honey. The thixotropic ratio varied from 1 to 100, the bell-heather honey having poor thixotropy. On a dry basis, the colloid pptd. by trichloroacetic acid ranged from 1.35 to 3.90 per cent. for the ling honeys and was 0.80 for the bell-heather honey. The average amount of N in the honey colloid was 10.25 per cent. Although a rough parallelism appears to exist between the thixotropy and the colloid content no exact relation was found.

A. O. JONES

234. A colorimetric method for the determination of invert sugar in the presence of sucrose using 2:3:5-triphenyltetrazolium chloride. A. Carruthers and A. E. Wootton (*Int. Sugar J.*, 1955, 57, 193-194).—*Procedure*—A sample of test soln. containing sucrose and 0.15 to 0.7 mg of invert sugar is made up to 4 ml with water, 1 ml of N NaOH and 1 ml of 1 per cent. 2:3:5-triphenyltetrazolium chloride solution are added and the tube is immediately placed in a bath of boiling water for 90 sec. The tube is then immersed in a bath of cold water and 1 ml of 1.1 N acetic acid is added; isopropanol is added, within 60 sec., up to nearly 20 ml, to dissolve all the pptd. formazan. The soln. is made up to exactly 20 ml, cooled, and the extinction is measured; a Hilger-Spekker instrument is used with blue-green filters and 0.25-cm cells. Invert-sugar concentrations can be determined from standard curves drawn up for 0, 0.2 and 0.4 g of sucrose present. Details are given for the preparation of raw juice and carbonatation juices for the test, as excess of lead and high alkalinity may affect the result.

SUGAR IND. ABSTR.

235. Control of molasses in sugar factories and refineries. G. Pidoux (*Ind. Alim. et Agric.*, 1955, 72, 395-401).—The importance of determining the percentage of crystals (x) in the molasses, when dealing with molasses which, as a result of poor crystallisation or a faulty centrifuge basket, contains fine crystals, is stressed. Several formulae for molasses purity, pol., ash, and sucrose content are quoted and their use for molasses containing fine crystals is discussed. A formula for x is given—

$$x = \frac{100(B' - B)}{100 - B}$$

where $B = ^\circ$ Brix of molasses containing crystals

and $B' = ^\circ$ Brix of molasses diluted with distilled water to dissolve the crystals (calculated to the same concn.) SUGAR IND. ABSTR.

236. A practical method, based on the technique of Khainovsky, for the analysis of milling.

L. R. Bliss (*Mem. XXVII Conf. Annual Assoc. T  cn. Azucar, Cuba*, 1953, 217-241).—The structure and composition of sugar cane and the behaviour of broken cells on treatment with imbibition water are discussed in detail. Khainovsky's method was based on the determination of the $^\circ$ Brix and polarisation of juice in the broken and unbroken cells, separately, in bagasse sampled after each milling stage, whereby the proportion of unbroken cells could be estimated in addition to evaluations of purities, etc. The juice was extracted from broken cells in cold water, air bubbles in cells being removed by repeated application and release of vacuum to the bagasse sample (1 kg) mixed with water (10 litres). In the modified method, for which an apparatus is used comprising a perforated copper basket contained within a steel cylinder with a side connection to a vacuum pump, and a reflux condenser (with upper stopper) at the top, the bagasse sample taken is 1 kg, with a water addition of $(6692 + 10f)$ ml of water, where $f =$ assumed percentage of fibre in bagasse; the pol. of the extract will then be equal to the pol. per cent. bagasse. After a cold extraction, and sampling of the solution for analyses, the water is heated by circulation through the pump to a heated copper coil and up to the top of the apparatus. The hot-extraction juice is then analysed as before. Khainovsky's results and their interpretation are discussed. The modified method is considered suitable for routine analyses.

SUGAR IND. ABSTR.

237. Determination of calcium salts [in sugar liquors] by the compleximetric method. G. S. Benin and S. L. Gutina (*Sakhar. Prom.*, 1954, 28 [4], 44-45).—The method of analysis by titration with EDTA (disodium salt) is applied to sugar liquors. The indicator used is Chromogen black.

SUGAR IND. ABSTR.

238. Determination of calcium salts [in sugar liquors] by the compleximetric method. F. N. Dobronravov and A. M. Gerasimova (*Sakhar. Prom.*, 1955, 29 [2], 20-21).—In the method of Benin and Gutina (*Anal. Abstr.*, 1956, 3, 237), Chromogen blue K and Chromogen dark blue were found to be better indicators than Chromogen black.

SUGAR IND. ABSTR.

239. The determination of the degree of acidity of flour. J. Terrier (Lab. Cantonal de Chim., Geneva, Switzerland) (*Mitt. Lebensmitt. Hyg., Bern*, 1955, 46 [3], 255-257).—A method is described for the successive determination of acidity due to organic and fatty acids, to phosphates, and to amino acids. *Procedure*—Weigh 5 g of flour into a centrifuge tube and agitate with 50 ml of peroxide-free ether for 5 min. Centrifuge, decant the extract and repeat the extraction; add an equal vol. of ethanol to the ethereal soln. and titrate with 0.1 N ethanolic KOH. Dry the residue and repeat the extraction with water; titrate the aqueous extract with 0.1 N NaOH, then add 10 ml of neutral 40 per cent. formaldehyde and again titrate with 0.1 N NaOH. Twice the sum of the three titres gives the degree of acidity.

W. H. PARR

240. Abnormally small freezing-point depressions of genuine milk. D. J. T. Bagnall and A. Smith (City Lab., Kingston-upon-Hull, England) (*Analyst*, 1955, **80**, 623-625).—Samples of milk taken under supervision from a herd of 32 cows (mainly Friesians, 19 of which had calved within 3 months of sampling) gave average freezing-point depressions as small as 0.518° and 0.522° C (Hortvet) for the morning and evening yields, respectively. The other analytical results suggest that these small depressions were due to deficiency of lactose caused by a recent change in the diet of the cows, when transferred from winter stall-feeding to grazing on lush spring grass. During a fortnight the freezing-point depression increased, and the lactose and other constituents of the milk regained their normal values. Reports of abnormally small depressions, such as these, for genuine milk are very rare, and a depression of 0.530° C (Hortvet) may still be generally regarded as the minimum depression for such milk.

A. O. JONES

241. Colorimetric method for estimation of lactose in milk. S. N. Mitra and J. K. Roy (School Trop. Med., Calcutta, India) (*J. Indian Chem. Soc., Ind. Ed.*, 1955, **18** [1], 34-38).—To 5 ml of clear milk serum are added 5 ml of standard FeCl_3 solution (1 ml = 0.1 g of Fe^{+++}) and 3 ml of Na_2CO_3 solution (1 ml = 20 mg of Na_2CO_3). The vol. is made up to 20 ml with water, the solution is then heated on a bath of boiling water for 25 min. and the residual Fe^{+++} are determined colorimetrically with NH_4SCN . The percentage of lactose is calculated by difference, i.e., on the amount of Fe^{+++} reduced. The method gives results that are 4 to 5 per cent. higher than those obtained by the Fehling method, but it is claimed to be useful for rapid routine work.

S.C.I. ABSTR.

242. Report on foreign fats in dairy products. A critical review of the Reichert - Meissl and Polenske determinations. S. D. Fine (Food and Drug Admin., Dept. Health, Denver, Colo., U.S.A.) (*J. Ass. Off. Agric. Chem.*, 1955, **38** [2], 319-338).—A glass-jointed apparatus is illustrated in detail, with dimensions. Reichert - Meissl and Polenske determinations were made on butter fat and on palm-kernel oil with this and the older (*Analyst*, 1936, **61**, 404) apparatus. The Reichert - Meissl value was not affected by the type of apparatus used, but the Polenske value, when high, was affected; hence the apparatus used must be specified. Gas heating is recommended, and carborundum is preferred to pumice as an anti-bumping agent. It is confirmed that varying pressure significantly affects the results, and it is noted that the method of extraction of butter fat from ice cream may also affect its Reichert - Meissl value. A. A. ELDRIDGE

243. A spectrophotometric method for the detection of certain stabilisers in soft curd cheeses. M. J. Gnagy (Food and Drug Admin., Dept. Health, Los Angeles, Calif., U.S.A.) (*J. Ass. Off. Agric. Chem.*, 1955, **38** [2], 189-193).—The gums are first separated by a lengthy procedure consisting essentially in removing the casein by treatment first with warm aq. NH_3 soln. and then with acetic acid, centrifuging and treating the filtrate with alcohol and $\text{KAl}(\text{SO}_4)_2$ soln. The residue is repeatedly treated with alcohol and $\text{KAl}(\text{SO}_4)_2$ soln., and is finally dissolved in hot aq. NH_3 . Acetic acid, followed by alcohol and $\text{KAl}(\text{SO}_4)_2$ soln., is then added; the ppt. is separated by centrifuging, dried, pulverised and refluxed with dilute HCl . The

resulting furfuraldehyde is steam-distilled and its extinction is measured in a spectrophotometer at 277.5 μm . Pectin, gum tragacanth, gum acacia and propylene glycol alginate can thus be detected at a concentration of 0.05 per cent., and algin and gum Karaya at a concentration of 0.1 per cent.

A. A. ELDRIDGE

244. A modified Cornell phosphatase test for the analysis of blue-mould and aged cheeses. J. H. Mahon, C. Anglin and R. A. Chapman (Dept. Nat. Health, Ottawa, Canada) (*J. Ass. Off. Agric. Chem.*, 1955, **38** [2], 482-493).—The Cornell phosphatase test (Kosikowsky, *Brit. Abstr. C*, 1952, 267) has been studied, and the procedure has been modified to improve the reproducibility of the results, to increase the linear range of the phenol calibration line, and to remove some anomalies in its application to blue-mould and aged cheeses. The slope of the phenol calibration line is depressed by all cheeses, and especially by aged cheese or blue-mould cheese. The effect is related to the free amino-acid content of the cheese. Higher phosphatase values are obtained by increasing the amount of 2:6-dichloro-quinonechlorimine reagent employed in the test. The use of a 1:6 dilution factor for all cheeses increases the slope, the analytical range, and the linearity of the phenol calibration line.

A. A. ELDRIDGE

245. The determination of starch in meat products with the anthrone reagent. F. J. Stevens and R. A. Chapman (Dept. Nat. Health, Ottawa, Canada) (*J. Ass. Off. Agric. Chem.*, 1955, **38** [2], 202-210).—The 5-g sample is treated with water (150 ml), zinc acetate solution (5 ml = 0.6 g) and $\text{K}_4\text{Fe}(\text{CN})_6$ solution (5 ml = 0.3 g). The mixture is set aside for 15 min., then centrifuged and filtered, and the residue is treated with 50 ml of the mixed reagent solutions (diluted 1:200). After filtration the treatment is repeated with 25 ml of the mixed reagent. The residue is then heated for 1 hr. in a water bath with 100 ml of 0.5 N H_2SO_4 , cooled, diluted to 200 ml, shaken and filtered. Of the filtrate 10 ml are diluted to 250 ml. A 2-ml aliquot of this solution is treated with 10 ml of anthrone reagent (0.2 g in 75 ml of conc. H_2SO_4 and 25 ml of water), cooled for 5 min., heated at 100° C for 10 min., and cooled again. The extinctions of this solution and of a standard glucose solution (0.2 g in 200 ml of water, diluted 1:25) are compared in an Evelyn colorimeter at 620 μm . Recoveries of added starch were \approx more 95 per cent. Glycogen or glucose present in liver interferes. The method does not always give consistent results. A. A. ELDRIDGE

246. Rapid determination of fat in meat products. H. Salwin, I. K. Bloch and J. H. Mitchell, jun. (Q.M. Food and Container Inst. Arm. Forces, Chicago, U.S.A.) (*J. Agric. Food Chem.*, 1955, **3** [7], 588-593).—A method for the rapid determination of fat (\approx 30 min.) in meat products is described. The ground sample of meat (9 g) is treated with perchloric-acetic acid mixture (30 ml) in a Babcock bottle and the bottle is immersed in a bath of boiling water until the meat sample is completely digested (\approx 12 min.); more of the acid mixture is added until the fat column rises into the calibrated neck when the bottle is centrifuged (2 min. at 875 r.p.m. at 1.5-inch diameter). Certain precautions in the use of perchloric acid are taken, 60 per cent. HClO_4 being recommended. Ten varieties of beef, veal and pork products were tested. Of 144 determinations by the rapid method, 143 agreed

with the A.O.A.C. method within ± 0.5 per cent. S.C.I. ABSTR.

247. Estimation of perchloroethylene (tetrachloroethylene) in fruit. J. Deshusses and P. Desbaumes (Lab. Cantonal de Chim., Geneva, Switzerland) (*Mitt. Lebensmitt. Hyg., Bern*, 1955, **46** [3], 233-237).—Tetrachloroethylene (I) is removed from the fruit in a current of air and passed through a tube electrically heated to between 900° and 1000° C. The HCl produced is absorbed in Na_2CO_3 soln. This soln. is then acidified with 10 per cent. HNO_3 and titrated with mercuric nitrate soln., diphenylcarbazone being used as indicator. Recoveries of added I were 99.94 ± 1.13 per cent. Analysis of fresh and imported dried fruits showed that I was absent. It disappeared rapidly from experimentally impregnated fruit. W. H. PARR

248. Contribution to the estimation of the diastatic power of malt and barley. H. Eschmann (Kantonales Lab., Berne, Switzerland) (*Mitt. Lebensmitt. Hyg., Bern*, 1955, **46** [3], 238-245).—Factors which affect the determination of the diastatic power of barley and malt have been examined. They include the amount of overheating which occurs during milling of the sample, the preparation of the mash and the quantity of NaOH used to stop saccharification. The following procedure is recommended. Place 20 g of carefully milled malt in a tared beaker with 500 ml of tap water at 40° C and keep at this temp. for 1 hr. Adjust to the original weight, cool and filter; discard the first 200 ml. Pipette 100 ml of starch soln. (2 per cent.) into a 200-ml calibrated flask and add 5 ml of acetate buffer (pH 4.3). Heat in a water bath at 20° C for 15 min., add 20 ml of the malt soln. and return to the bath for a further 30 min. Add 2 ml of N NaOH and make up to the mark. Carry out a blank omitting the malt soln. Determine the maltose by the compleximetric method of Poterat and Eschmann (*Anal. Abstr.*, 1955, **2**, 1327). An accuracy to within 2 to 3 LMB-units is claimed. W. H. PARR

249. Determination of traces of nickel in malt beverages. M. Kenigsberg and I. Stone (Wallerstein Lab., New York, U.S.A.) (*Anal. Chem.*, 1955, **27** [8], 1339-1340).—The method involves evaporation of the beer or wort to dryness with HCl (1:1), followed by dry ashing in a muffle furnace at $\approx 500^\circ\text{C}$. The ash is dissolved in dil. HCl and is extracted with a CCl_4 soln. of dithizone to remove Cu and Fe. The aq. phase is treated with dimethylglyoxime and bromine water and then made alkaline with ammonia to develop the red to brown colour due to Ni, the intensity of which is measured in a photometer. Recoveries of added Ni are between 80 and 110 per cent. at the 0.04 to 0.4 p.p.m. level. Reproducibility is good. G. P. COOK

250. Rapid methods for the determination of total hop bitter substances (iso-compounds) in beer. F. L. Rigby and J. L. Bethune (Canadian Breweries Ltd., Toronto) (*J. Inst. Brew.*, 1955, **61** [New Series 52] [4], 325-332).—Two methods are described, one suitable for most routine purposes, and a second giving greater accuracy. (1) A sample of beer (50 g), not degassed, is weighed directly into a 500-ml flask, and acidified with 7.5 ml of 6 N HCl. 2:2:4-Trimethylpentane (50 ml) is added, the glass stopper is inserted and the flask rotated for 1 min.; the stopper is raised momentarily and the shaking is continued for 15 min. The soln.

is set aside for 5 min., then the lower layer (mostly beer) is drawn off and discarded. The remaining emulsion is centrifuged, 5 ml of the trimethylpentane layer are transferred by pipette into a 25-ml flask, made up to vol. with methanol containing 0.2 ml of 1.5 N NaOH per 100 ml, and read at 255 m μ . Extinction $\times 96.15$ = apparent iso-compound concentration, mg per kg of beer. The apparent values, which are ≈ 30 per cent. too high, are reduced to real values by a regression equation. The reliability of the values obtained has been established by comparison with countercurrent distribution values for the same samples of beer. (2) The beer is extracted with trimethylpentane as in method (1). The extract is centrifuged, then 15 ml of the clear trimethylpentane phase are transferred, by pipette, to a 50-ml glass-stoppered cylinder containing 15 ml of acidified methanol (6.8 vol. of methanol and 3.2 vol. of 4 N HCl). The cylinder is stoppered and the phases are equilibrated by inverting the cylinder 100 times at a rate of ≈ 2 sec. per inversion. The phases are allowed to separate and a 5-ml aliquot of the trimethylpentane is diluted and read in the spectrophotometer as in method (1). S.C.I. ABSTR.

251. Determination of free and total sulphur dioxide in white table wines. M. A. Joslyn (Univ. of California, Berkeley, U.S.A.) (*J. Agric. Food Chem.*, 1955, **3** [8], 686-695).—Two methods for the determination of free and total SO_2 by iodimetric titration and the fuchsine-formaldehyde colorimetric method were critically examined for factors affecting accuracy and reproducibility of the results, e.g., in the first method the concentration of the starch affected the sharpness of the end-point and the speed of titration affected the reproducibility of the results. The standard procedure was to pipette aliquots of wine into 250-ml glass-stoppered flasks and then to add N NaOH quickly. After being mixed, the soln. was allowed to stand for the required time, then quickly acidified with N HCl. The following modifications were made. The iodine titration was first made using 0.5 to 1.0 ml of 0.5 per cent. sol. starch soln.; subsequently 5 ml of 1 per cent. starch soln. were added. Approx. 0.01 N iodine soln. was run in rapidly from a 10-ml microburette with vigorous shaking and then added, dropwise, until a blue colour persisted for 0.5 min. In the second method, the concentration of the H_2SO_4 had the greatest effect on sensitivity. The Steigman reagent, prepared by adding 0.100 g of basic fuchsine wetted with 5 ml of 95 per cent. ethanol, to a 500-ml volumetric flask containing 25 ml of a soln. of concentrated (66° Bé) H_2SO_4 in 450 ml of water and then diluting to vol., was stable for several months. S.C.I. ABSTR.

252. Microbiological assay of mesoinositol using *Kloeckera apiculata* and *Saccharomyces veronae*: application to grapes and wines. J. Ribereau-Gayon, E. Peynaud and S. Lafourcade (*Rev. Ferment. Ind. Aliment.*, 1955, **10** [3], 119-121).—Four series of tubes, each containing 10 ml of culture medium (composition stated) and added amounts of mesoinositol (I), varying from 0.25 to 2.5 μg , were each inoculated with one of each of the following: *K. apiculata* (II), *Sacch. veronae* (III), and *Torulopsis bacillaris* 46 and 61. Each tube was incubated for 40 hr. at 25° C and the optical density was then determined with an absorptiometer. The relation between the content of I and optical density was found to be linear with II and III. The technique was applied to the assay of I in wines and in grape

juices during the ripening period. Wine should be de-sulphited, diluted (1:1000) with distilled water, and samples of 1, 2, 3 and 4 ml used for the assay as described above. Alternatively, the wine may be clarified with Pb acetate (neutral) and I pptd. with basic Pb acetate in ammoniacal solution, re-dissolving the ppt. in aq. H_2SO_4 , separating from $PbSO_4$ by filtration, and diluting the filtrate and washings to a suitable aliquot. S.C.I. ABSTR.

253. Paper-chromatographic examination of sugars used for improving wine. I. Qualitative examinations of sugars derived from starch. H. Thaler (Dtsch. Forschung. Lebensmittelchem., Munich, Ger.) (*Z. Lebensmitt. Untersuch.*, 1955, **100** [5], 359-366).—The qualitative compositions of three brands of starch-sugars (almost pure glucose, used for improving wine) were analysed by paper chromatography. Gentioibiose, isomaltose and a trisaccharide—reversion products formed through acid hydrolysis—as well as higher oligosaccharides, which are not subject to fermentation, were easily detected on chromatograms, made by eluting 0.05 ml of wine with a mixture of *n*-propanol-ethyl acetate-water (6:1:3) for 15 to 24 hr. The spots of reducing sugars, on air-dried paper, were sprayed with acid *p*-anisidine phthalate (1.23 g of *p*-anisidine and 1.66 g of phthalic acid in 100 ml of 96 per cent. alcohol) and dried at 105°C. Reducing hexoses and oligosaccharides gave brown, pentoses red and galacturonic acid yellow to orange spots.

S.C.I. ABSTR.

254. Determination of higher alcohols in spirituous liquors. J. Lafon and P. Couillaud (*Ann. Falsif.*, 1955, **48**, 273-282).—The methods for determining the higher alcohols in spirits, due to Rocques (*Ann. Chim. Anal.*, 1897, 142), and Guymon and Nakagiri (*Proc. Amer. Soc. Enol.*, 1952, **3**, 117), are examined. The Rocques method is to eliminate aldehydes and to add to 10 ml of spirit, distilled to 66.7 per cent. of ethanol, 10 ml of conc. H_2SO_4 and allow to stand for 1 hr. at 120°C. The yellow-brown colour developed is compared with standards derived from an alcoholic solution containing 1 g per litre of isobutyl alcohol. It is now recommended that the time of standing be 2 hr., that the test sample should be diluted to give a higher alcohol content, > 250 g per hectolitre, and that the temp. of standing should be carefully controlled. The Guymon-Nakagiri method, a modification of that due to Komarowsky, is regarded as preferable. It comprises the addition, to 1 ml of distillate, of 20 ml of H_2SO_4 containing 0.5 g per litre of dimethylaminobenzaldehyde, heating at 100°C for 20 min., and comparing with standards at 520 $m\mu$.

S.C.I. ABSTR.

255. Some observations on the colorimetric determination of vanillin. D. T. Englis, J. W. Miles and L. A. Wollerman (Univ. Illinois, Urbana, Ill., U.S.A.) (*J. Ass. Off. Agric. Chem.*, 1955, **38** [2], 519-523).—The formation of a ppt. on addition of the Na_2CO_3 solution in the Folin-Denis method for the colorimetric determination of vanillin can be rendered less likely by reducing the amount of Na_2CO_3 employed, or prevented by addition of a small amount of sodium hexametaphosphate with the usual amount of Na_2CO_3 . In the latter method slightly higher extinctions were observed.

A. A. ELDRIDGE

256. Detection of foreign animal fats in chicken-fat. C. Franzke (*Z. Lebensmitt. Untersuch.*, 1955, **102** [2], 81-84).—The constants of the fat are

determined for the purpose of detecting beef or pork in chicken-meat in samples where histological or serological methods are inapplicable, owing to the previous comminution and heating of the meat. Beef fat and lard on the one hand, and chicken-fat on the other, are much better distinguished by the differences between yields of polybromides obtained from their unsaturated acids than by the differences between their iodine values. A still sharper distinction is obtained by the spectrophotometric determination of the extinction values at 233 $m\mu$ of the alkali-isomerised fatty acids. Full directions are given for the determination of the polybromides, which are formed by the addition of 5 per cent. Br in light petroleum (v/v) to a soln. of the fatty acids in the same solvent at -8°C.

P. S. ARUP

257. The purification of milligram quantities of vitamin A. L. T. Powell, R. F. Krause and P. L. Sanders (Sch. Med., W. Virginia Univ., Morgantown, Va., U.S.A.) (*Arch. Biochem. Biophys.*, 1955, **57** [2], 306-311).—The procedure described is intended primarily for use in isotope-dilution studies. Interfering substances are removed by double pptn. with digitonin and by chromatography on alumina; spectroscopically pure vitamin A is obtained in 68 to 69 per cent. yield from light-petroleum extracts of liver.

W. H. C. SHAW

258. A highly specific procedure for ascorbic acid. M. X. Sullivan and H. C. N. Clarke (Georgetown Univ., Washington, D.C., U.S.A.) (*J. Ass. Off. Agric. Chem.*, 1955, **38** [2], 514-518).—The method depends on the reduction of $FeCl_3$ by ascorbic acid and the colorimetric determination of the $FeCl_2$ by means of reaction with $\alpha\alpha'$ -dipyridyl; the reaction is carried out in the presence of H_3PO_4 to eliminate interference by reductone. A solution (1 ml) containing ≈ 0.02 mg of ascorbic acid is treated with 0.3 ml of 85 per cent. H_3PO_4 to give a pH of 1 to 2, 5 ml of 0.5 per cent. $\alpha\alpha'$ -dipyridyl soln. and 1 ml of 1 per cent. $FeCl_3$. The method has been applied to orange juice, honey and urine; it is sensitive to 5 μg of ascorbic acid per ml.

A. A. ELDRIDGE

259. Rapid method of dehydroascorbic acid reduction for total vitamin-C determination. E. Piyanowski (*Przem. Rolny Spozywczy*, 1954, **11**, 410-415).—Reduction is effected by adding *M* sodium sulphide soln., acidified with HCl, and removing the excess of sulphide with *M* ethanolic $HgCl_2$ soln. Reduction is complete in 10 to 15 min. Clear filtrates are readily obtainable for titration with dichlorophenolindophenol.

N. E.

260. Separation and determination of phosphate esters of thiamine by paper electrophoresis. N. Siliprandi and D. Siliprandi (Univ. Rome) (*Riv. Ist. Sieroter. Ital.*, 1954, **29**, 361-365).—Electrophoresis on paper has been used to separate and determine thiamine and its mono-, di-, tri- and poly-phosphate esters. Munktel No. 20 paper, 10 cm \times 34 cm, was wetted with Na acetate-acetic acid buffer (pH 5.2), blotted, and placed on a plastic plate between two electrolyte vessels so that it dipped in each; 0.005 ml of an aq. soln. of 50 to 150 μg of mixed thiamine and esters was placed midway on the paper. A current of 20 mA at 200 V was passed for 3 hr. After drying at 80°C, development was done with 2 ml of 2 per cent. $K_3Fe(CN)_6$ in 50 ml of 30 per cent. aq. NaOH and 50 ml of 95 per cent. ethanol. Blue-fluorescing spots were seen in u.v. light at 366 $m\mu$. Thiamine moved further towards the

cathode than the monophosphate; polyphosphate moved furthest towards the anode, triphosphate less and diphosphate least. For quant. results, spots after being dried were located with u.v. light at 253.6 m μ , eluted with buffer soln. and the absorption read at 270 m μ .
CHEM. ABSTR.

261. New method for the quantitative determination of thiamine. P. Rőzsa (*Magyar Kém. Foly.*, 1955, **61** [4], 122-125).—The 4-amino-2-methylpyrimidine group in thiamine (aneurine) is hydrolysed with H₂SO₄ to give NH₃; by alkaline fission of the thiazole ring and subsequent oxidation to SO₄²⁻, the S can also be determined. *Procedure*.—Extract the thiamine from tablets with methanol and ethanol (distilled from KOH); transfer a sample containing 10 to 20 mg of thiamine to another flask, remove the alcohol and dissolve the dry residue in 50 per cent. H₂SO₄ (5 ml) and heat over a small flame for 1 hr. Cool, wash the condenser with H₂O (2 ml), add 1 drop of methyl red and attach the flask to the Schulek - Vastagh ammonia-distillation apparatus (*Z. anal. Chem.*, 1931, **84**, 167). The receiver contains 0.02 N H₂SO₄ (10 ml) and the dropping funnel CO₂-free 10 per cent. aq. NaOH. Start the distillation; when all the air has been expelled, add the alkali dropwise until the soln. turns yellow and then an additional 1 ml. Continue the distillation until bumping starts; the volume is then \approx 15 ml. Boil the distillate until free from CO₂ and titrate the excess of acid with 0.02 N NaOH. Wash the residue from the distilling flask with H₂O (5 \times 5 ml) into a bromination flask, add KBr (1 g) and 0.1 N KBrO₃ (10 ml), acidify rapidly with 38 per cent. HCl (10 ml) and stopper the flask. After 60 min., cool and add 5 per cent. aq. KI (10 ml) and titrate with 0.1 N Na₂S₂O₃. If 50 per cent. H₂SO₄ is used, the time of oxidation is only 30 min. and only 5 \times 3 ml of H₂O are used for washing. 1 ml of 0.02 N H₂SO₄ = 6.743 mg, and 1 ml of 0.1 N KBrO₃ = 4.214 mg of thiamine. The two sulphur determinations give identical results, and the sulphur and nitrogen methods agree within 1 per cent. A. G. PETO

262. Polarographic determination of nicotinamide alone and in mixtures with nicotinic acid. R. Cernătescu, M. Poni and R. Ralea (*Studii și Cercetări Stiin.*, 1953, **4** [1-4], 117-124; *Referativnii Zh.*, *Khim.*, 1955, Abstr. No. 7,706).—In a supporting electrolyte of 0.1 N NaCl or KCl soln., the polarographic wave of nicotinamide (I) occurs at \approx -1.6 V, and that of nicotinic acid (II) at \approx -1.2 V. A mixture of I and II gives two well-defined waves whose heights are not equal to the heights of the waves obtained with the pure compounds. When the soln. is made alkaline with KOH, the wave of II disappears and that of I remains, and its height corresponds to the concn. of I. The usual polarographic methods for the determination of II are inaccurate in the presence of I. E. HAYES

263. Electrophoretic separation and determination of flavins. P. Cerletti and N. Siliprandi (*Biochem. J.*, 1955, **61** [2], 324-328).—A method is described for the separation and determination of riboflavin and its derivatives (flavin mononucleotide, flavin-adenine dinucleotide, lumichrome and lumiflavin) by paper electrophoresis. The flavins are then eluted and determined photofluorimetrically or spectrophotometrically at 260 and 450 m μ . Although the fluorescence readings are low, owing to quenching, a correction can be applied, and fluorimetry is preferred, because it is 30 times more

sensitive than spectrophotometry at 260 m μ . The paper-electrophoresis method has high resolving power and gives sharp and readily reproducible separation.
J. N. ASHLEY

264. A study of the yeast method for vitamin B₆. W. P. Parish, H. W. Loy, jun., and O. L. Kline (Food and Drug Admin., Dept. Health, Washington, D.C., U.S.A.) (*J. Ass. Off. Agric. Chem.*, 1955, **38** [2], 506-513).—The method of Atkin, Schultz, Williams and Frey (*Ind. Eng. Chem.*, 1943, **15**, 141), in which *Saccharomyces carlsbergensis* is used, has been modified to increase the sensitivity. A more dilute inoculum (\approx 0.008 mg of moist yeast cells) is employed, and the inoculum is grown in the assay medium under the conditions of the assay. The assay solutions and the basal medium are sterilised separately and added together under aseptic conditions. Uniformity of agitation during incubation at 25°C for 22 to 28 hr. is improved by placing a glass bead in each assay tube. Under these conditions the response of yeast to pyridoxal was equal to that to pyridoxine, but growth with pyridoxamine was 50 to 60 per cent. of that with pyridoxine.
A. A. ELDRIDGE

265. Microbiological detection of preservatives in foods. M. J. Bernaerts (*Conserva.*, 1955, **4** [2], 38-42).—Available techniques and their applications in testing various foods are briefly described; their advantages and limitations are discussed, with special reference to their occasional inadequacy for detecting amounts as small as 0.35 to < 0.7 p.p.m. (as Hg) of organomercury compounds in beer. Growth-inhibiting factors that may occur in jams or preserved fruits are concn. of sugar high enough to affect the growth of osmophilic yeasts used as test-organisms, or growth-inhibiting substances that may be naturally occurring or formed, e.g., by the oxidation of limonene or by the heating of sugar soln. In testing preserved fruit products, dilution of the sample and increases in the amounts of test-organisms used for inoculation are recommended. Although these techniques must be classed as presumptive tests, requiring further standardisation, their wider adoption is recommended. P. S. ARUP

See also Abstract 129.

Sanitation

266. Electrochemical determination of oxygen concentration in surface waters. F. Tödt, W. Schwarz and H. G. Todt (*Gesundheitsing.*, 1954, **75**, 224-226).—Difficulties in the application of the electrochemical method of determining oxygen in surface waters are due mainly to variations in the concn. of NaCl and Ca(HCO₃)₂. Variations in the concn. of NaCl cause variations in voltage drop across the electrolyte, resulting in displacement of the cathode potential and alteration of the current. The effect of the concn. of Ca(HCO₃)₂ is that in the alkaline cathode space CaCO₃ is formed, which settles on the cathode surface and reduces the electrochemically active surface. Favourable conditions were obtained by using Hg or noble-metal amalgams of given compositions.

WATER POLLUTION ABSTR.

267. Determination of sulphate ion in natural water containing large amounts of ferri and ferrous ions. Kiyoharu Isagai (Saga Univ.) (*Japan Analyst.*, 1955, **4** [3], 171-172).—The determination of SO₄²⁻ in natural water by titration, with sodium rhodizonate as indicator, is markedly affected by Fe²⁺ and

Fe⁺⁺⁺. This interference can be eliminated by removing both Fe⁺⁺ and Fe⁺⁺⁺ with the aid of the ion-exchange resin Amberlite IR-120(Na). The sample soln. is passed through a column of resin, the eluate is treated with a known amount of BaCl₂ soln., and the excess is titrated with standard H₂SO₄ soln., a 0.1 per cent. soln. of sodium rhodizonate (5 drops) being used as indicator. The presence of small amounts of ethanol (5 drops) and NH₄Cl (5 per cent., 5 drops) gives a sharp end-point.

K. SAITO

268. **The analysis of sea water. A review.** H. Barnes (Marine Stn., Millport, Isle of Cumbrae, Scotland) (*Analyst*, 1955, **80**, 573-592).—A review is given of the results of analyses of sea water and attention is drawn to some of the analytical problems involved. The principles are given of the analytical methods that have been used for the "conservative" elements and ions, Na, K, Ca, Mg, Sr, SO₄²⁻, Br, B and F. Methods available for determination of the "non-conservative" nutrient elements are discussed, particularly P, N, Si, organic carbon and the micro-nutrients Fe, Mn and Cu. (159 references.)

A. O. JONES

269. **A modification of the 1-naphthylamine-sulphanilic acid method for the determination of nitrites in low concentration [in waters].** H. D. Zeller (Univ. Missouri, Columbia, Miss., U.S.A.) (*Analyst*, 1955, **80**, 632-633).—To overcome difficulties in the determination of low concn. of NO₂⁻ in limnological work, a modification of the standard colorimetric method has been developed. When the colour has been developed in the usual way with sulphanilic acid and 1-naphthylamine acetate, NaCl is added to saturation and the coloured complex is extracted with quantities (4, 3 and 3 ml) of *n*-butanol. The combined extracts are examined with a photo-electric colorimeter with a green filter and the concn. of NO₂⁻ is ascertained from a calibration graph. The method is not applicable to concn. of NO₂⁻ > 0.02 p.p.m.

A. O. JONES

270. **Measurement of atmospheric pollution by ultra-violet photometry.** D. J. Troy (E. I. du Pont de Nemours and Co., Wilmington, Del., U.S.A.) (*Anal. Chem.*, 1955, **27** [8], 1217-1221).—A portable u.v. gas and vapour analyser based on Hanson's design (*Ind. Eng. Chem., Anal.*, 1941, **13**, 119) is described. It is sensitive to Hg, O₃, C₂H₄ and its derivatives, ketones, chlorinated ethylenes and SO₂, all of which absorb strongly at 254 mμ, and to NO₂, CS₂, Cl and Br, which absorb strongly at other wavelengths. The instrument consists principally of a u.v. source having 80 per cent. of its measurable radiation at 254 mμ, a double-beam optical system, vacuum-phototube detector and a sensitive, stable electronic micro-ammeter. Calibration problems are discussed and a continuous-flow calibrating apparatus is described.

K. A. PROCTOR

271. **Colorimetric determination of carbon monoxide in air by an improved palladium chloride method.** T. H. Allen and W. S. Root (Columbia Univ., New York, U.S.A.) (*J. Biol. Chem.*, 1955, **216** [1], 309-317).—Christman's method (*Brit. Abstr. B*, 1937, 733) for the determination of CO in air by the reduction of PdCl₂ has been considerably improved. The addition of KI converts the un-reduced PdCl₂ into PdI₂, and the optical density of the pinkish-red solution is determined spectrophotometrically at 490 mμ. A formula is given for the calculation of the amount of CO. Concn.

of CO from 94.2 to 0.010 per cent. and less can be determined on 100 ml of air. J. N. ASHLEY

272. **The phenol coefficient number as an index to the practical use-dilution for disinfection.** L. S. Stuart, L. F. Ortenzo and J. L. Friedl (Agric. Res. Service, U.S. Dept. Agric., Washington, D.C., U.S.A.) (*J. Ass. Off. Agric. Chem.*, 1955, **38** [2], 465-478).—The relation between concentration and germicidal activity is exponential in character but is not simple. A nomogram for converting phenol coefficient numbers to effective dilutions for disinfecting is presented. A. A. ELDRIDGE

273. **Modified "pyrethrin II" assay.** W. Mitchell and F. H. Tresadern (Stafford Allen and Sons, Ltd., London, England) (*J. Sci. Food Agric.*, 1955, **6** [8], 465-467).—An additional stage in the A.O.A.C. (or Seil) method for the determination of "pyrethrin II" is recommended: the chrysanthemum-dicarboxylic acid, being readily sol. in boiling water, is separated from water-insol. acidic matter before titration. The residue, after evaporation of the ether, is boiled with distilled water (75 ml) and filtered hot. The residues in the dish and filter-paper are washed with boiling water (< five 20-ml portions) until the filtrates are neutral to litmus. The combined filtrates are titrated with 0.02 N NaOH to phenolphthalein. The accuracy of the "pyrethrin II" determination is improved.

S.C.I. ABSTR.

274. **Polarographic determination of 3-(2-acetyl-1-phenylethyl)-4-hydroxycoumarin (Warfarin).** J. Kováč (*Chem. Zvesti*, 1954, **8** [6], 342-345; *Referativnyi Zh., Khim.*, 1955, Abstr. No. 7,702).—An indirect polarographic method for the determination of Warfarin is based on the formation of CHI₃ when the -COCH₃ group reacts with an alkaline soln. of iodine. The ppt. of CHI₃ is filtered off, dissolved in methanol and determined polarographically. The CHI₃ equivalent of Warfarin is determined empirically. In the analysis of technical products, a preliminary polarographic determination of benzylidenacetone, which also reacts with alkaline iodine soln. to form iodoform, should be made.

E. HAYES

See also Abstracts 148, 181.

Agriculture and Plant Biochemistry

275. **Colorimetric determination of phosphorus in plant materials.** A. J. Cavell (Nat. Agric. Adv. Serv., Wolverhampton, England) (*J. Sci. Food Agric.*, 1955, **6** [8], 479-480).—Phosphorus in plant extracts can be accurately determined colorimetrically as the yellow molybdovanadophosphate by using a mixed solution of ammonium vanadate and ammonium molybdate (I) (5 g of ammonium molybdate and 0.25 g of ammonium vanadate dissolved in warm water, cooled, diluted to 500 ml and filtered). (See *Anal. Abstr.*, 1954, **1**, 1993.) *Procedure*—The ash of the material (5 g) is moistened with 5 ml of conc. HCl, evaporated to dryness and the silica is dehydrated at 105° C. The residue is boiled gently with 5 ml of conc. HCl for 2 min., then 25 ml of water are added. The product is boiled, filtered through a 9-cm Whatman No. 30 paper, and the filtrate and washings are made up to 250 ml. A 10-ml aliquot is transferred by pipette into a 50-ml calibrated flask, 10 ml of 5 N HCl are added, and the soln. is diluted to 50 ml with water to give a final acidity of ≈ N. A 5-ml

aliquot of this solution is transferred by pipette into a dry glass-stoppered tube, which is placed in a water bath at 20° C for 5 min. and, at this temp., 5 ml of **I** are added. The solutions are mixed, held at 20° C for 5 min. and read at 400 m μ with an SP600 Unicam spectrophotometer, 1-cm cells being used.

S.C.I. ABSTR.

276. Determination of reducing compounds in cellulose hydrolysates. G. N. La Diega (Univ. Palermo, Sicily) (*Ann. Chim., Roma*, 1954, **44**, 168-182).—The methods of (i) Willstaetter and Schudel, (ii) Shaffer and Somogyi, and (iii) Bertrand for the determination of glucose (alone or with added sodium sulphate) are evaluated. It is shown that the standing times and titration periods, after neutralisation of the alkaline oxidation mixtures, must be standardised, and that the free acidity during titration requires careful control. In greater quantities, sodium sulphate inhibits oxidation and interferes with the titration; correction curves are given. The presence of reducible decomposition products of glucose also produces errors (high glucose values). A cellulose hydrolysate with polymer fractions of high molecular weight ($\alpha = 30$ per cent.) shows, although free from glucose decomposition products, the same interference on analysis with added sodium sulphate. For cellulose hydrolysates with varying molecular weight, different values are found by methods (ii) and (iii). All three methods can be used for studying acid hydrolysis (at H₂SO₄: cellulose ratios of 1 and 2), the most accurate results being obtained by method (i).

BRIT. COTTON IND. RES. ASS. ABSTR.

277. Reduction of nitrate by ferrous hydroxide under various conditions of alkalinity. J. M. Bremner and K. Shaw (Rothamsted Exptl. Stn., England) (*Analyst*, 1955, **80**, 626-627).—Low results were obtained in the determination of NO₃⁻ by reduction to NH₃ with reduced Fe and H₂SO₄ at room temp., the NH₃ being determined by diffusion with MgO in a Conway micro-diffusion unit at 18° to 25° C. A series of expt. suggested that some of the reduction occurs after the liquid has been made alkaline for the distillation of NH₃, the residual reduction being effected by the Fe(OH)₂ then formed. It was shown also that determination of NH₃ by distillation with MgO of solutions containing significant amounts of NO₃⁻ may give erroneously high results, if appreciable amounts of Fe⁺⁺ are present. In the conventional method for the determination of NH₃ in soil by extraction with acid N KCl and distilling the extract with MgO (Olsen, *Brit. Chem. Abstr. B*, 1929, 951), the amount of Fe extracted is too low to cause interference by NO₃⁻. Distillation of vol. of 300 ml (containing 1 mg of NO₃⁻ and different amounts of FeSO₄) with MgO for 30 min. showed that no reduction of NO₃⁻ occurred when the concn. of Fe⁺⁺ was 70 mg per litre and that quant. reduction occurred when it was 7 g per litre.

A. O. JONES

278. Phthalein complexone as an indicator for calcium and magnesium in the titration of soil extracts. B. M. Tucker (Waite Agric. Res. Inst., Adelaide) (*J. Aust. Inst. Agric. Sci.*, 1955, **21**, 100-101).—The sum of exchangeable calcium and magnesium in soil extracts may be determined by titration with disodium EDTA. If Eriochrome black T is used as an indicator for Mg, traces of Cu, Co, etc., give coloured complexes with the indicator, which may be oxidised if Mn is present.

Phthalein complexone, developed by Anderegg *et al.* (*Anal. Abstr.*, 1954, **1**, 1180), is very sensitive to alkaline-earth and Mg ions and is not affected by these other metals. The colour change is from a violet-red to pale pink. The residual pink colour may be masked more effectively by Naphthol green B than by the mixture of methyl red and Diamine green B recommended by Anderegg *et al.*

S.C.I. ABSTR.

279. Determination of calcium carbonate equivalence of limestone and dolomite through potentiometric titration to pH 7. W. M. Shaw, B. Robinson and W. H. MacIntire (Univ. Tennessee Agr. Exp. Stn., Knoxville, Tenn., U.S.A.) (*J. Ass. Off. Agric. Chem.*, 1955, **38** [2], 240-245).—Certain dolomites, when boiled with HCl and back-titrated with NaOH, give CaCO₃ values below those indicated by direct determination of Ca and Mg, owing to obscuring and absorptive effects of the Fe, Al and Mn present. The procedure of "Official Methods of Analysis," 7th Ed., Washington, D.C., 1950, is therefore modified; 0.25 N NaOH is added rapidly to attain pH 5 and then dropwise to attain pH 7 and remain constant, with stirring, for 1 min.

A. A. ELDRIDGE

280. Infra-red determination of dieldrin and DDT in mixtures. G. E. Pollard, W. M. Saltman and P. Yin (Shell Chem. Corp., Denver, Colo., U.S.A.) (*J. Ass. Off. Agric. Chem.*, 1955, **38** [2], 478-482).—The sample, containing 10 g of toxicant, is added to a Celite column 25 to 50 mm long, and percolated with three 50-ml portions of CS₂ containing 5 per cent. of acetone. The extract is evaporated on a steam-bath and the residue, after being heated at 75° C for 15 min., is dissolved in CS₂ to 100 ml. The absorbance is determined at 10.96 and 14.06 μ in a Perkin-Elmer model 12C infra-red spectrophotometer calibrated against the two substances separately. Equations for calculation of the results are given.

A. A. ELDRIDGE

281. Chromatographic 2:4-dinitrophenylhydrazine method for determination of allethrin. N. Green and M. S. Schechter (U.S. Dept. Agric., Beltsville, Md., U.S.A.) (*Anal. Chem.*, 1955, **27** [8], 1261-1265).—The method is based on the conversion of allethrin to the 2:4-dinitrophenylhydrazine derivative, which is separated on a silicic acid column and is determined by gravimetric or colorimetric means. About 0.002 mole of the sample is treated with 0.003 mole of 2:4-dinitrophenylhydrazine (**I**) in 50 ml of anhydrous methanol containing 0.25 ml of conc. HCl. The mixture is set aside for 2.5 hr. with occasional swirling and the derivative is extracted into benzene. An aliquot which has been concentrated by evaporation is introduced on to a silicic acid - Hyflo Super-Cel (2:1) column and is eluted with a mixture of benzene, Skellysolve B and ether (50:50:3, by vol.). The band for the phenylhydrazine derivative is usually rather wide and diffuse and is easily followed down the column visually; the band is collected, the solvent is evaporated and the residue dried to constant weight. Alternatively, the fraction is measured colorimetrically at 375 m μ . Results from the gravimetric method agree well with those from the ethylenediamine method on commercial samples; the colorimetric procedure is accurate to ± 10 per cent.

G. P. COOK

282. Infra-red spectrophotometric determination of allethrin. S. K. Freeman (Benzol Products Co., Newark, N.J., U.S.A.) (*Anal. Chem.*, 1955, **27** [8],

1268-1274).—Allethrin is determined by measurement of the 5.81- μ band, a wavelength at which only allethrolone of the four impurities in the insecticide interfere. The sample is dissolved in CCl_4 and the allethrin content is measured by reference to a standard curve. The infra-red absorption spectra of possible impurities—allethrolone, and chrysanthemum-monocarboxylic acid and its chloride and anhydride—were studied and their spectra are illustrated. The 5.56- μ band was used for measuring the anhydride, and allethrolone can be determined by means of its 2.86- μ absorption max., both standard and differential techniques for this being described. *cis*- and *trans*-Allethrins exhibit different absorptivities at 5.81 μ and the relative quantities are measured by their extinctions at 8.70 and 8.85 μ . More than 50 commercial allethrin samples were analysed and 12 representative analyses are listed. Results were in close agreement with those from a chemical method in which ethylenediamine was used, the one exception differing by 0.8 per cent. on assay. G. P. COOK

283. Analysis of some new pesticides. R. Suter, R. Delley and R. Meyer (J. R. Geigy, Basel, Switzerland) (*Z. anal. Chem.*, 1955, **147** [3], 173-184).—*Diazinon*—Macro quantities of diazinon [OO-diethyl O-4-methyl-2-isopropylpyrimid-6-yl thiophosphate] (I) are assayed by dissolving in ether, washing with H_2O and 0.05 N NaOH, drying, evaporating and titrating the residue with HClO_4 in glacial acetic acid. Methods are given for the determination of the following impurities: total bases (including I) by direct titration with HClO_4 ; 6-mercapto-4-methyl-2-isopropylpyrimidine and 6-hydroxy-4-methyl-2-isopropylpyrimidine by extraction from the water washings in the assay of I with ether in acid soln. and CHCl_3 in neutral soln., respectively, and titration with HClO_4 ; total acids (calculated as diethyl hydrogen thiophosphate) by titration with NaOH in 50 per cent. alcohol; mono- and di-ethyl thiophosphoryl chlorides by oxidation with peroxide in alcoholic soln., acidification, washing with light petroleum and electro-metric titration of Cl^- with AgNO_3 ; triethyl thiophosphate by extraction of an acid soln. with ether, washing with acid, alkali and H_2O , evaporation, and weighing the residue; ethyl di-(4-methyl-2-isopropylpyrimid-6-yl) thiophosphate by paper chromatography and u.v. spectrophotometry; and benzene by u.v. spectrophotometry. Methods are given for the preliminary extraction of I from such products as powders, sprays and pastes; adsorption on alumina is used if simpler methods fail. On the micro scale (*e.g.*, in milk), I is assayed by hydrolysis with HBr and colorimetric determination of the liberated H_2S as methylene blue. Assays involving u.v. and i.r. spectrophotometry and pptn. with heteropolyacids have also been studied. *Chlorbenzilate*—Macro quantities of chlorbenzilate (ethyl 4:4'-dichlorobenzilate) (II) are assayed by saponification of the ester group or by acetylation of the hydroxyl group. Powders, fumigation papers, etc., are assayed by Soxhlet extraction, followed by saponification or determination of Cl^- . Micro quantities are concentrated by saponification and removal of fatty acids by filtration, and determined by conversion into 4:4'-dichloro-3:5:3':5'-tetranitrobenzophenone, which gives a red colour with sodium methoxide. *Isolan*—Macro quantities of Isolan (3-methyl-1-isopropylpyrazol-5-yl dimethylcarbamate) are assayed by acid hydrolysis, distillation of the alkaline soln. and titration of dimethylamine in the distillate. Powders may require preliminary

extraction with ether. On the micro scale, the dimethylamine is determined colorimetrically as copper dimethyldithiocarbamate. A. R. ROGERS

284. Pre-assay purification of tissue extracts by wax column [for determination of insecticides]. W. R. Erwin, D. Schiller and W. M. Hoskins (Univ. California, Berkeley, Calif., U.S.A.) (*J. Agric. Food Chem.*, 1955, **3**, 676-679).—A method is described for removing interfering substances which have been extracted from plant or animal tissues in the determination of residues of org. insecticides. A column consisting of finely ground alumina (80 to 200 mesh) coated with a mixture (2:1) of white soft paraffin and paraffin wax (m.p. 160° to 165° F) is used. The column is eluted with aq. methyl cyanide (60 per cent.), but a separation of the toxicants may be effected by the successive use of 40, 60 and 75 per cent. soln. Recovery of toxicant is satisfactory (*e.g.*, 90 to 100 per cent. for DDT, Toxaphene, etc., from spinach). S.C.I. ABSTR.

See also Abstracts 67, 68, 84, 109, 168, 169, 252, 293.

5.—GENERAL TECHNIQUE AND LABORATORY APPARATUS

General

285. Protecting alkali in automatic burettes from carbon dioxide. C. O. Ingamells (189 Erindale Ave., Hamilton, Ontario) (*Chemist Analyst*, 1955, **44** [3], 83).—A soda-lime tube is used at the air inlet of the burette. When the chamber enclosing the levelling device at the top of the measuring tube is vented by a tiny hole, a flask lined, by the method given, with $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ is inverted over the burette top. O. M. WHITTON

286. Simple instrument for titrimetry without indicators. Gas pressure end-point technique. VIII. Acid-base reactions. O. R. Gottlieb (Orinstein and Cia., Rio de Janeiro) (*Anal. Chim. Acta*, 1955, **13** [2], 101-107).—Titrations are conducted in a closed system, the top of the titration flask being connected to the space at the top of the burette by a capillary tube, a branch of which forms a U-tube manometer. The top of the burette bears a glass stopper that permits release of pressure. Continuous magnetic stirring is used. When an acid soln. is titrated with standard NaOH (containing a trace of Na_2CO_3) an increase of pressure is obtained at each addition of titrant until the end-point is reached; after this point a contraction is observed. Acids can also be titrated with standard Na_2CO_3 , and hydroxides, carbonates, bicarbonates or their mixtures can be titrated with standard acid by observing the beginning or cessation of gas evolution. Solutions of concn. ≤ 0.01 N can be used. The accuracy is similar to that obtained with indicators, but the method can be applied to solutions that are coloured or contain suspended solids. W. C. JOHNSON

287. Soxhlet apparatus for working under reduced pressure. W. Ensslin (*Z. anal. Chem.*, 1955, **146** [5], 321-322).—A modification of the usual Soxhlet extraction apparatus is described, so that the extraction is carried out under reduced pressure. The extraction vessel is contained in a jacket through which water or other cooling medium is circulated. A. J. MEE

288. **Laboratory apparatus for recovery of solvents in extractions.** H. Demus (*Chem. Tech., Berlin*, 1954, 6 [10], 552).—A heated evaporating tower for removal and recovery of liquid from extraction residues is described. It consists essentially of a double-walled iron tube with inlets and outlets for vapours or hot liquids; the outer wall reduces heat losses. A rack for holding glass dishes when removing solvent is also described.

D. R. GLASSON

289. **A new apparatus for the rapid determination of carbon.** I. Sajo (Iron Industry Res. Inst., Budapest) (*Magyar Kém. Foly.*, 1955, 61 [1], 9-13).—A detailed description is given of an apparatus and a process suitable for the rapid determination ($1\frac{1}{2}$ to 2 min., after weighing) of C in steel, slag, etc. The sample (e.g., 1 g of steel shavings) is burnt in O in a high-frequency furnace, or with PbO_2 (0.2 to 0.3 g), and the gases are collected in a special burette. A fixed volume of the gas is then passed through a KOH bubbler into a second burette, which is built inside the other one. The carbon content (percentage) is read directly on a suitable series of scales. The accuracy is comparable with that of the older methods. The same principle can be used for the determination of other gases, with accuracy equal to that of the Orsat apparatus, but less time is required.

A. G. PETO

290. **A simple apparatus for automatically controlling the distillation of fluorine as fluorosilicic acid.** E. D. Schall and H. G. Williamson (Purdue Univ., Lafayette, Ind., U.S.A.) (*J. Ass. Off. Agric. Chem.*, 1955, 38 [2], 452-454).—In the apparatus, which is illustrated, the mercury thermo-regulator closes the input circuit of the relay when the temperature rises above the selected value; the solenoid valve then admits water to the distillation mixture. As the solution cools the relay input circuit is opened and the valve closes. With a capillary tube capable of delivering 15 to 20 ml of water per min. an automatic temperature control of $\pm 1^\circ$ C is attained.

A. A. ELDRIDGE

291. **Simple automatic apparatus for the distillation of fluorine as fluorosilicic acid.** J. K. Johannesson (*N. Z. J. Sci. Tech.*, 1955, 36 [B] [6], 636-639).—A thermostatic device is described to control the rate of heat application to the distilling flask by a steady rate of addition of steam, and is primarily designed for use in the estimation of fluorides in water by distillation as H_2SiF_6 . The apparatus consists of a small 0.5-ml bulb blown at the end of a length of Pyrex-glass tube (6 mm outside diameter), which is then bent through 180° just below the bulb. The tube is inserted through the stopper in the mouth of the flask, which also carries a thermometer and a steam-delivery tube. The Pyrex-glass tube and bulb are filled with clean Hg, and one drop (0.05 ml) of an appropriate org. liquid with a small air-bubble (0.01 ml) is introduced into the bulb by inverting and tapping. The org. liquids used were various mixtures of toluene and xylene. The criterion of selection is to give a mixture whose v.p. will increase sufficiently at the max. desired temp. to cut off the heat supply. An electrical cut-off operating a commercial gas solenoid valve is also shown.

S.C.I. ABSTR.

292. **Apparatus for the determination of carbamic acid derivatives.** R. Payfer (Dept. Agric., Ottawa, Canada) (*J. Ass. Off. Agric. Chem.*, 1955, 38 [2], 534-536).—The apparatus, which consists of a

4-bulb Allihn condenser, flask, 10-bulb scrubber, and 5 wash-bottles, can be used for the determination of isopropyl phenylcarbamate (Gard, *Anal. Chem.*, 1951, 23, 1685); the mixture of H_3PO_4 and H_2SO_4 is boiled and cooled before use, and three of the wash-bottles contain 0.1 N NaOH. For the determination of dithiocarbamate, the absorbing solutions are 10 per cent. lead acetate and 2 N ethanolic KOH.

A. A. ELDRIDGE

293. **Use of a mechanical mixer in preparing fertiliser samples for analysis.** H. R. Allen (Kentucky Agric. Exp. Stn., Lexington, Ky., U.S.A.) (*J. Ass. Off. Agric. Chem.*, 1955, 38 [2], 460-464).—The mixer holds two large containers for mixing the unground sample and two smaller ones for mixing portions after grinding. With samples containing less than 30 units of plant food, a one-pint sample could be obtained directly from the mixing chamber with a scoop. When mixtures contained > 30 units the presence of ingredients varying greatly in particle size made it necessary to spread out the sample and take portions from a number of places.

A. A. ELDRIDGE

294. **Continuous paper-chromatography.** J. Solms (Agrikulturchem. Inst., Zürich) (*Helv. Chim. Acta*, 1955, 38 [5], 1127-1133).—A new apparatus is described and illustrated. A sheet of chromatographic paper, rolled into a cylinder, is adjusted round a circular elution trough so that its top edge, cut into uniform strips and bent inwards, is in contact with the eluting agent in the trough, which is automatically replenished from a reservoir. The lower edge of the paper is serrated to facilitate drainage. The mixture to be separated is continuously supplied from another reservoir, and is applied to the paper by means of a capillary tube. The amount applied is regulated by the intermediary siphoning action of filter-paper strips, varying in thickness and width according to the quantities required. During the process of separation the cylinder is rotated perpendicularly to the elution current. The components on the paper are thus agitated in two directions vertical to each other and their eluates are drained into removable receptacles, mounted below the cylinder. The process is demonstrated by separations of LiCl and KCl, xylose and galactose, and methylene blue and fuchsine. An aq. solution (≈ 0.21 ml) containing 12.3 per cent. of LiCl and 5.4 per cent. of KCl was eluted with methanol in 50.3 hr. at 20° C. The speed of rotation was 1.3 cm per hr. The R_F values found were LiCl 0.55 and KCl 0.18.

S.C.I. ABSTR.

295. **Inexpensive glass chamber for one- and two-dimensional ascending paper-chromatography.** T. Miwa and H. Zeitlin (Univ. Hawaii, Honolulu) (*Anal. Chem.*, 1955, 27 [8], 1357).—The construction of a glass chamber (12 in. \times 24 in. \times 24 in.) for use in ascending paper-chromatography, with five single-weight window panes, is described. The use of weather stripping in its construction allows the escape of sufficient volatile solvent to prevent undue sweating and condensation without impairing efficiency. The results obtained by its use are said to be excellent and reproducible.

K. A. PROCTOR

296. **Recording gel tester.** E. T. Hjermstad (*Cereal Chem.*, 1955, 32 [3], 200-207).—An automatic method of measuring the deformation under increasing load and the yield point of gels is

described and illustrated. In this, a device is used which lowers a gel containing an embedded disc at a slow uniform rate; the disc is attached by a cord to a dynamometer capable of registering the desired range of force. As the gel is slowly lowered, the dynamometer reacts upwards with increasing force on the disc until the yield point of the gel is reached.

S.C.I. ABSTR.

297. Rapid gas analyser using ionisation by alpha particles. P. F. Deisler, jun., K. W. McHenry, jun., and R. H. Wilhelm (Princeton Univ., N.J., U.S.A.) (*Anal. Chem.*, 1955, **27** [9], 1366-1374).—A method and apparatus are described for the analysis of a flowing or quiescent gaseous mixture, which is ionised by α -particles from Po in an aged radium-D source. Binary systems, H-N, H-ethylene, ethylene-ethane, N-CO₂, and the ternary N-H-ethane have been analysed satisfactorily, $n-1$ independent measurements being necessary for a mixture of n components. In principle, gases of different molecular, atomic and electronic structure should be differentiated by this method, exceptions thus being ortho-H-para-H, H-D. Precision of analysis in the prototype apparatus was about 0.2 to 0.3 mole per cent. for binary mixtures.

K. A. PROCTOR

298. Sampling for in-line instrumentation. A degasser for obtaining air-free samples. U. L. Upson (General Electric Co., Washington, U.S.A.) (*Anal. Chem.*, 1955, **27** [9], 1443-1445).—A de-gassing device is described for use with aqueous or organic sample streams containing up to 98 per cent. of air. It operates in the flow range obtainable with an air jet of 8 cu. ft. per min. and delivers a sample stream of at least 99.95 per cent. liquid content, comprising 50 to 80 per cent. of the liquid content of the input stream. A minimum liquid-input flow of 0.05 gal. per min. is required when an air flow of < 0.5 gal. per min. is involved. At air-flow rates of 0.5 to 1 gal. per min., the liquid input can be as low as 0.015 gal. per min. For a liquid input of 0.05 to 1 gal. per min., air contents up to 2 gal. per min. can be tolerated. Special designs and modifications for specific, unusual applications are discussed.

K. A. PROCTOR

See also Abstracts 13, 16, 177.

Optical

299. The stability and sensitivity of instruments used in spectrophotometric analysis. C. Morton (*J. Pharm. Pharmacol.*, 1955, **7** [8], 541-548).—The power required for the amplifier and tungsten lamp of the Unicam SP500 photo-electric spectrometer may be derived from mains with the aid of a bridge voltage-regulator (using barretters); readings are unaffected by changes of ± 50 per cent. in the voltage of the power supply or by variations in frequency. A 12-fold increase in the overall sensitivity of the spectrophotometer, together with a substantial improvement in zero stability, may be achieved by replacing the 600- μ A galvanometer by a 50- μ A meter, at the same time providing a counter-current of about 300 μ A.

A. R. ROGERS

300. Light sources for spectrum analysis. V. High-voltage spectrographic spark source with electronic control. A. Bardócz (Ungar. Akad. Wiss., Budapest) (*Acta Tech. Acad. Sci. Hung.*, 1954, **8**, 99-107).—A fixed spark gap and thyatron-tube

circuit control the spark source. The thyatron tube initiates the discharge and is controlled by a pulse generator. The charging voltage of the condenser does not pass through the thyatron tube but is uniformly distributed between the controlling and analytical gaps. The current flow is started by a pulse to the thyatron tube, which causes first the controlling spark gap and then the analytical gap to spark over. Finally, the entire condenser energy passes through the two spark gaps. Characteristic operation curves are given. CHEM. ABSTR.

301. Investigation of light sources for spectral analysis. An electronically controlled spark generator. A. Bardócz (Ungar. Akad. Wiss., Budapest) (*Acta Phys. Acad. Sci. Hung.*, 1954, **4**, 90-120).—A review of electronically controlled spark sources, including the author's own thyatron-controlled spark generators (see *Anal. Abstr.*, 1956, **3**, 300), is given. Diagrams of circuit parameters and performance characteristics are given. Oscillograms of controlled spark pulses are also shown. (80 references.)

CHEM. ABSTR.

302. Forms of electrode and their use in emission spectroscopic analysis. H. Svejda (*Öst. Chem. Ztg.*, 1954, **55** [9-10], 117-127).—The types of electrodes used in emission spectroscopic analysis are reviewed. The shapes in which a solid sample can be fashioned as an electrode are listed and their suitability is discussed. Mention is also made of electrodes formed from metal sheet, wire and turnings, and from briquetted material. Carrier electrodes are described that are suitable for solid material, powders and solutions. Micro-analyses by means of emission spectroscopy are also discussed.

J. H. WATON

303. Reduction of rapid random fluctuations of the Beckman flame spectrophotometer. C. F. Rothe (Ohio State Univ., Columbus, Ohio, U.S.A.) (*Anal. Chem.*, 1955, **27** [9], 1507).—A circuit is described in which condensers are fixed across the null-meter of a Beckman DU spectrophotometer to reduce the rapid random fluctuations which occur when this instrument, with direct-atomsing flame-attachment and photomultiplier, is used at near-max. sensitivity of the photomultiplier. The replacement of the sensitivity and dark current control knobs by turns-counting Duodials, model RB (Beckman Instruments) leads to more rapid and accurate resetting of the controls. K. A. PROCTOR

304. Double-beam method of spectral selection with flames. C. T. J. Alkemade and J. M. W. Milatz (*J. Opt. Soc. Amer.*, 1955, **45** [7], 583-584).—An absorptiometer system is described, based on the double-beam principle, in which the absorption "cell" is a flame containing the vapour of the element to be determined. The flame is placed in one of the two light beams, which are periodically chopped in opposite phase. A photo-multiplier connected to a synchronous measuring circuit determines the out-of-balance of the system. Radiation emitted by the flame does not interfere, since it is not modulated to the detector system. It is suggested that this method may be of value in determinations that are difficult to carry out by conventional flame photometry, owing to spectral interference.

B. S. COOPER

305. High-temperature recording polarimeter. R. S. Saltzman, J. F. Arbogast and R. H. Osborn (Hercules Powder Co., Wilmington, Delaware,

U.S.A.) (*Anal. Chem.*, 1955, **27** [9], 1446-1448).—A recording photo-electric polarimeter, used to monitor continuously the optical rotation of a plant screen of molten resin at 180° C, is described. It has been in use for over two years and has proved to be very stable and to have an overall accuracy of within about 1 per cent. A balanced electrical network containing two photocells is arranged so that a change in optical rotation creates an unbalanced signal which, in turn, after amplification, actuates the balance motor of a recorder. This motor simultaneously moves the recorder pen and rotates a polariser in the instrument until balance is restored. K. A. PROCTOR

306. **Stroboscope polarimeter.** G. F. Landegren (*Rev. Sci. Instrum.*, 1955, **26** [6], 578-579).—Light passes successively through a rotating Polaroid disc and a stationary Polaroid disc thus producing sinusoidally modulated light which is incident on a phototube. After amplification the resulting signal is fed to a stroboscope directed on to the rotating disc which carries a degree scale, the zero mark of which is adjusted to appear to coincide with a stationary mark. The interposition of an optically active sample between the two Polaroid discs causes a phase shift in the modulation of the light and a reading, observed in stroboscopic light, on the rotating disc. G. SKIRROW

See also Abstract 270.

Thermal

307. **The temperature control of laboratory apparatus.** I. K. A. Galloway (*Lab. Practice*, 1955, **4** [7], 283-287).—Basic principles of temperature control are considered. Types of controller, e.g., rheostat, multi-heat switch, variable transformer, energy regulator, thermostat, thermo-regulator, controlling pyrometer and resistance thermometer, and their relative merits are described. Subsidiary factors in temperature control are discussed. O. M. WHITTON

308. **Studies in bomb calorimetry. III. Determination of heat capacity (water equivalent) of bomb-calorimeter system. IV. Corrections.** J. E. Barker, R. A. Mott and W. C. Thomas (Brit. Coke Res. Assoc., London) (*Fuel, Lond.*, 1955, **34** [3], 283-302, 305-316).—In all determinations of heat capacity (*H*) and calorific value (*C*) conditions should be uniform for the amount of water in the calorimeter vessel, the mean calorimeter temp. (θ), the initial oxygen pressure (*P*), the total heat release, the length of igniting cotton and the firing wire. Formulae are given to correct the specific heats of water and metals to values at $\theta = 25^\circ \text{C}$ and the heat of combustion of benzoic acid to $P = 30 \text{ atm}$. To ensure complete combustion the dried benzoic acid must be briquetted. The no. of tests required to fix the value of *H* within ± 3 , ± 2 and $\pm 1 \text{ cal.}$ are 6, 14 and 54, respectively. With 14 tests the possible error in *C* due to inaccuracy in *H* is $\approx 10 \text{ B.Th.U. per lb.}$ For the cooling correction the pre-firing and final periods must be extended until observations over 5 min. show rates of temp. change with a max. average deviation $> 0.00072^\circ \text{C per min.}$ for *C*, or $> 0.00048^\circ \text{C per min.}$ for *H*. The correction for the formation of aq. H_2SO_4 from SO_2 is $2.265 \text{ cal. per mg of S.}$ The HNO_3 correction may be taken as $10.2 \pm 1.4 \text{ cal.}$ in a total heat release of 7500 cal. for all except very slow or very fast burning fuels. The ejection of ash during

combustion is avoided by using a crucible of Ni-Cr foil tapering upward. The thermometer should be calibrated at 0.2°C intervals and used preferably over the same range in all tests. The use of resistance thermometers is being investigated.

A. R. PEARSON

309. **Rotating blade-stirrer and small-sample technique in the determination of freezing points.** W. C. Crawford and C. L. A. Harbourn (Brit. Petroleum Co. Ltd., Sunbury on Thames, England) (*Anal. Chem.*, 1955, **27** [9], 1449-1451).—Two new stirrers are described for the determination of f.p. The first was applied to the measurement of the m.p. of organic sulphur compounds and the second to samples as small as 8 ml, enabling an accuracy of $\pm 0.01^\circ \text{C}$ and the corresponding f.p. for the pure substance to be calculated with an accuracy of $\pm 0.1^\circ \text{C}$. G. P. COOK

310. **Automatic instrumental methods for determination of critical solution temperatures.** J. R. Mosley, C. A. Lucchesi and R. H. Muller (Univ. California, Los Alamos, New Mexico, U.S.A.) (*Anal. Chem.*, 1955, **27** [9], 1440-1443).—Several instrumental methods of determining critical soln. temp. using photo-electric detection and control are described. Schmitt trigger circuits or limit switches mounted in standard recorders are used for heater control; the temp. is recorded on standard recording potentiometers. The precision attainable is about $\pm 0.05^\circ \text{C}$. K. A. PROCTOR

Electrical

311. **Constant-current sources based on transistors.** N. H. Furman, L. J. Sayegh and R. N. Adams (Princeton Univ., N.J., U.S.A.) (*Anal. Chem.*, 1955, **27** [9], 1423-1425).—The characteristics of some electrical circuits based on the use of a germanium transistor of the p-n-p junction type and designed to deliver a small constant current are discussed. Close temp. control is necessary. After a 15-min. warming-up period, the stability of a constant-current unit is from 0.02 per cent. to better than 0.01 per cent. for the range $100 \mu\text{A}$ to 5 mA, and changes in load resistance from 0 to 100 ohms produce a change of 0.01 to 0.1 per cent. in current output. The advantages of transistors are long life, stability to shock, comparative low power requirements and simplified circuits. K. A. PROCTOR

312. **Electrochromatography. VII. Separation of ions by means of organic solvents.** Masabumi Maki (Japan Women's Univ.) (*Japan Analyst*, 1955, **4** [3], 156-158).—The electrophoretic separation (400 V, 3 hr.) of common ions was studied in methanol containing NH_4Cl (0.0005 mole per litre) and a methanol-acetone mixture containing HCl (0.05 N). The ionic mobilities were entirely different from those in an aqueous soln. and were dependent on the composition of the solvent. The separation of the spot of Sr^{++} from that of Ba^{++} , and of Zn^{++} from Ni^{++} , Co^{++} and Mn^{++} , which is difficult in aqueous soln., can be readily effected in methanol-acetone mixture. K. SAITO

313. **Polarography with a mercury-pool cathode in stirred solutions.** D. J. Rosie and W. D. Cooke (Cornell Univ., Ithaca, N.Y., U.S.A.) (*Anal. Chem.*, 1955, **27** [9], 1360-1363).—To extend the polarography of solutions to the micromolar range, the

use of a large mercury-pool cathode in a stirred solution was investigated and found to be suitable. The sensitivity is about 300 times greater than that of the dropping electrode. The mercury pool has an area of 3 sq. cm and uses 3 ml of Hg per run. Variations in cell geometry and stirring rate influence the magnitude of the diffusion current and must therefore be standardised. The polarograms have the same shape as those obtained with a dropping electrode, but have no maxima (in some instances, anomalous unexplained peaks have been obtained) and are independent of the scanning rate. The current fluctuations caused by the drop growth are absent. Over a period of one month, the average deviation of 17 runs on $10^{-5} M$ *o*-nitrotoluene was 2.4 per cent. and of 13 runs on $10^{-8} M$ Cd⁺⁺ was 3.1 per cent.

K. A. PROCTOR

314. An electromagnetic vibrator for electrodes used in polarography and amperometric titrations. A. J. Lindsey (Sir John Cass College, London) (*Anal. Chim. Acta*, 1955, **13** [2], 200-202).—The vibrator contains a guide to centre the electrode and to restrict the vibrating motion to one direction only. The constructional details are illustrated.

W. C. JOHNSON

315. Silver electrode. C. L. Gordon (Nat. Bur. Stand., Washington, D.C., U.S.A.) (*Anal. Chem.*, 1955, **27** [9], 1508).—The preparation of a sturdy silver electrode, which can be easily re-surfaced, is described. The electrode is also useful in instances when a small known area is required.

K. A. PROCTOR

316. Potentiometric titration by a new method. J. Dévay and M. Béres (*Magyar Kém. Foly.*, 1955, **61** [5], 134-135).—By this method the second derivative $\Delta^2 E / \Delta V^2$ of $E = f(V)$ is measured. The retarded and the indicator electrodes are connected through a leak-proof oil-condenser ($6 \mu F$), a resistance, a galvanometer (sensitivity 10^{-9} amp.) and a tapping key. The soln. was mechanically stirred and the titrant was added in small and equal portions. After each addition the key was depressed to observe the direction of the current, and the soln. round the retarded electrode was mixed. The deflection of the galvanometer is reversed when the p.d. across the condenser is greater than between the two electrodes, i.e., when $\Delta E / \Delta V$ starts to fall. The method was used for $0.1 N Cl^- - AgNO_3$ and $Fe^{II} - KMnO_4 - H_2SO_4$ systems, using 0.01-ml increments; their volume and some electrical factors determine the accuracy; in this instance it was 0.01 ml. The magnitude of the resistance in the circuit does not matter; when it is absent, the resistance of the electrolyte soln. ($\approx 18,000 \Omega$ for the argentimetric and 200Ω for the redox system) was sufficient to prevent polarisation.

A. G. PETO

317. A transistor amplifier for the dead-stop end-point. J. B. Phillips (Univ. Louisville, Kentucky, U.S.A.) (*Chemist Analyst*, 1955, **44** [3], 80-81).—When the transistor amplifier illustrated is connected in place of the galvanometer in the usual dead-stop circuit, the current is amplified six or seven times and thus a micro-ammeter may be used rather than a galvanometer. The circuit

is very stable with negligible drain on the battery. Fifteen titrations of a $Na_2S_2O_3$ solution with 0.1001 N iodine solution gave an average deviation of 0.00006 with amplification and an average deviation of 0.0003 without amplification. The amplifier may also be used in amperometric titrations.

O. M. WHITTON

318. A new coulometric cell. W. Fuchs and W. Quadt (Chem.-techn. Inst., Techn. Hochsch., Aachen, Germany) (*Z. anal. Chem.*, 1955, **147** [3], 184-195).—An electrolytic cell is described for the continuous production of soln. of H^+ free from OH^- , or of OH^- or I^- free from H^+ (compare the cell of Pitts *et al.*, *Anal. Abstr.*, 1954, **1**, 1819). For producing soln. of OH^- from Na_2SO_4 soln., the cathode compartment is separated from the anode by a clay tube (through which the electrolyte flows) round the anode, and contains $BaCO_3$ or a cation-exchange resin to remove H^+ as they are formed. For soln. of I^- from KI soln., a cation-exchange resin is used similarly. For soln. of H^+ , the signs of the electrodes are reversed; with Na_2SO_4 soln., the anode compartment contains an anion-exchange resin, or $MgSO_4$ can be used as electrolyte to remove OH^- as $Mg(OH)_2$. Numerous titrations of HCl with electrolytically produced OH^- , of $NaOH$ with H^+ , and of arsenite with I^- , in which a visual or potentiometric end-point is compared with the coulometric figure, indicate an accuracy of ± 0.4 per cent.

A. R. ROGERS

319. Application of coulometric titrations to micro volumes of solution. R. Schreiber and W. D. Cooke (Cornell Univ., Ithaca, N.Y., U.S.A.) (*Anal. Chem.*, 1955, **27** [9], 1475-1476).—A general coulometric technique, applicable to a variety of titrations and using ≈ 0.01 ml of soln. is described. The accuracy is said to be comparable to that of conventional methods.

K. A. PROCTOR

320. The problem of leaks in vacuum techniques. Utilisation of a mass spectrometer as a leak detector. R. Geller (*Rapp. Centre Ét. Nucl. Saclay*, 1954, No. 325, 98 pp.).—The problem of leakage and its detection in vacuum systems is examined both practically and in terms of mathematical theory. A method of leak detection, based on the use of a helium mass-spectrometer, and the apparatus used are described in detail.

S.C.I. ABSTR.

321. Determination of the concentration of radioactive aerosols emitting α -particles. J. Labeyrie (*Rapp. Centre Ét. Nucl. Saclay*, 1954, No. 335, 120 pp.).—Techniques are described for the quant. measurement of concentration of aerosols containing radioactive emanations, emitting α -particles, of both short- and long-life periods. The estimation of Rn in air by activity determinations on airborne dusts, particularly with samples containing U_3O_8 and hydrated Fe_2O_3 (limonite), was studied. Data resulting from the determination of Ra and Th emanations in Paris air are given: $^{222}Rn = 1.3$ to 11.0×10^{-10} ; $^{220}Rn = 4.5$ to 40.0×10^{-12} curie per cu. metre.

S.C.I. ABSTR.

See also Abstract 19.

ABBREVIATIONS

Certain abbreviations in everyday use are not included in the following list. When any doubt might arise from the use in the text of an abbreviation or symbol the word is printed in full.

| | | | |
|--------------------------------------|-------------------|---|---------------|
| alternating current | a.c. | millicurie | mC |
| ampere | amp. | milligram | mg |
| Angstrom unit | Å | millilitre | ml |
| anhydrous | anhyd. | millimetre | mm |
| approximate, -ly | approx. | millimicron | mμ |
| aqueous | aq. | millivolt | mV |
| atmospher -e, -ic | atm. | minimum | min. |
| boiling-point | b.p. | minute (time) | min. |
| British thermal unit | B.Th.U. | molar (concentration) | M |
| calorie (large) | kg-cal. | molecul -e, -ar | mol. |
| calorie (small) | g-cal. | normal (concentration) | N |
| centimetre | cm | number | no. |
| coefficient | coeff. | observed | (obs.) |
| concentrated | conc. | ounce | oz |
| concentration | concn. | part | pt. |
| critical | crit. | patent | pat. |
| crystalline | { | parts per million | p.p.m. |
| crystallised | | per cent. wt. in wt. | per cent. w/w |
| cubic | cu. | per cent. wt. in vol. | per cent. w/v |
| current density | c.d. | per cent. vol. in vol. | per cent. v/v |
| cycles per second | c.p.s. | potential difference | p.d. |
| decompos -ing, -ition | (decomp.) | pound | lb |
| density | ρ | precipitate | ppt. |
| density, relative | d or wt. per ml | precipitated | pptd. |
| derivative | deriv. | precipitating | pptg. |
| dilute | dil. | precipitation | pptn. |
| direct current | d.c. | preparation | prep. |
| distilled | dist. | qualitative, -ly | qual. |
| electromotive force | e.m.f. | quantitative, -ly | quant. |
| electron-volt | eV | recrystallised | recryst. |
| equivalent | equiv. | refractive index | n |
| experiment | expt. | relative humidity | R.H. |
| foot, feet | ft. | revolutions per minute | r.p.m. |
| gram | g | saponification value | sap. val. |
| gram-molecule | mole | saturated calomel electrode | S.C.E. |
| half-wave potential | E ₁ | second (time) | sec. |
| horse-power | h.p. | soluble | sol. |
| hour | hr. | solution | soln. |
| hydrogen ion concentration | [H ⁺] | specific gravity | sp. gr |
| hydrogen ion exponent | pH | specific rotation | [α] |
| inch | in. | square centimetre | sq. cm |
| infra-red | i.r. | standard temperature and pressure | s.t.p. |
| insoluble | insol. | temperature | temp. |
| kilogram | kg | ultra-violet | u.v. |
| kilovolt | kV | vapour density | v.d. |
| kilowatt | kW | vapour pressure | v.p. |
| maxim -um, -a | max | volt | V |
| melting-point | m.p. | volume | vol. |
| microcurie | μC | watt | W |
| microgram | μg | wavelength | λ |
| microlitre | μl | weight | wt. |
| micron | μ | | |
| milliamper | mA | | |

In addition the following symbols are used—

| | | | |
|------------------------------|---|--|---|
| greater than | > | less than | < |
| not greater than | ≥ | not less than | ≤ |
| is proportional to | α | of the order of, approximately | ≈ |

The principal Pharmacopoeias are denoted by B.P., U.S.P., or D.A.B., together with the identifying numeral.

Radicles are represented by the usual symbols; positive ions have superscript dots and negative ions superscript dashes, e.g., Cu⁺⁺, Al⁺⁺⁺, Cl⁻, SO₄⁻. Metals that exist in more than one valency state are represented by their symbols with appropriate superscript roman numerals, e.g., ferric iron becomes Fe^{III} and cuprous copper Cu^I.

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